Novel and Efficient Azomethine Ylide Forming Photoreactions of *N*-(Silylmethyl)phthalimides and Related Acid and Alcohol Derivatives

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Received October 28, 1994[⊗]

Abstract: An investigation of the photochemistry of *N*-(silylmethyl)phthalimides and related α-phthaloylacetic acids and 2-phenylethanol derivatives has uncovered new excited state processes resulting in the formation of azomethine ylide intermediates. Irradiation of *N*-[(trimethylsilyl)methyl]phthalimide in MeCN promotes C to O silyl transfer to generate the corresponding azomethine ylide which is efficiently trapped by reaction with water to yield the *N*-methylphthalimide or by dipolar cycloaddition with acetone, methyl acrylate, or acrylonitrile. Cycloadditions with the latter two dipolarophiles are both regioselective and endo-stereoselective. These processes can be triplet photosensitized by use of acetophenone. The related *N*-[(trimethylsilyl)methyl]-1,8-naphthalimide reacts in a similar manner upon irradiation in MeCN solutions containing the dipolarophiles methyl acrylate and acrylonitrile to produce cycloadducts which undergo spontaneous elimination of TMSOH, yielding α,β-unsaturated ester or nitrile products. The ylide formed by irradiation of the (silylmethyl)phthalimide is trapped in a stereospecific (retention) manner by the dipolarophiles *trans*-hex-4-en-3-one, dimethyl maleate, and dimethyl fumarate. The effect of aryl ring substitution on the regiochemical course of the photoinduced C to O silyl migration process was probed by use of the 4-methoxy- and 4-carbomethoxyl-*N*-(silylmethyl)phthalimides. Irradiation of the former substance in an MeCN solution containing acrylonitrile gives rise to a single adduct whose structure suggests that silyl migration to oxygen of the carbonyl meta to the OMe substituent is highly favored. In contrast, the 4-carbomethoxyphthalimide is converted under these conditions to a mixture of regioisomeric adducts. Thus, silyl migration in the excited state of this substance is nonselective. In accord with hints found in earlier observations made by Kanaoka (*Chem. Pharm. Bull.* **1982**, *30*, 1263), *N*-phthalimide derivatives of the α-amino acids glycine, alanine, and phenylalanine undergo similar ylide forming photoreactions upon irradiation in MeCN solutions. The azomethine ylides produced by photodecarboxylation of these substances are efficiently trapped by dipolarophiles, and the overall photoreactions starting with the alanine and phenylalanine derivatives are highly stereoselective. Finally, the *N*-phthalimide derivative of 2-amino-1-phenylethanol also is transformed to a related ylide upon irradiation in MeCN. The nature, regiochemical and stereochemical course, and mechanistic interpretation of these new azomethine ylide forming photoreactions are discussed in this publication.

Introduction

Past studies of phthalimide photochemistry have shown that these substances participate in a number of mechanistically interesting excited state processes.[1] For example, phthalimide singlet and triplet excited states have been found to undergo H-atom abstraction reactions with the intramolecular examples (*i.e.*, Norrish type-II processes) displaying the typical preference for the γ-position.[2] Thus, as is the case with other carbonyl compounds,[3] the excited states of these substances have oxy-radical character. In addition, excited states of phthalimides have modestly high reduction potentials, and consequently, they are strong oxidizing agents. As a result, SET-promoted photoreactions of phthalimides with arene, thioether, ether, and amine donors are common.[4] Finally, phthalimides undergo photoinduced cycloaddition reactions with those olefins which cannot serve as good electron donors.[5] The cycloaddition processes suggest that phthalimide singlet excited states have a large C−N π-bond order (see below).

Our interest in this well-studied area of photochemistry was stimulated recently by the congruence of thoughts about a number of issues related to phthalimide excited state reactivity. The first concerns questions about the potential for SET-promoted photoreactions of *N*-(silylalkyl)phthalimides. It is now

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⊗ Abstract published in *Advance ACS Abstracts,* February 15, 1995.

(1) (a) Coyle, J. D. *Synthetic Organic Photochemistry*; Hospool, W. M., Ed.; Plenum Press: New York, 1984. (b) Mazzocchi, P. H. *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1981; Vol. 5.

(2) (a) Kanaoka, Y.; Yoshida, K.; Hatanaka, Y. *J. Org. Chem.* **1979**, *44*, 664. (b) Kanaoka, Y. *Acc. Chem. Res.* **1978**, *11*, 407. (c) Kanaoka, Y.; Kayama, K.; Flippen, J. L.; Karle, I. L.; Witkop, B. *J. Am. Chem. Soc.* **1974**, *96*, 4719. (d) Coyle, J. D.; Harriman, A.; Newport, G. L. *J. Chem. Soc., Perkin Trans. 2* **1979**, 799.

(3) Wagner, P. J. *Top. Curr. Chem.* 1973, *66*, 1. Wagner, P. J. *Rearrangements in Ground and Excited States*; deMayo, P., Ed.; Academic Press: New York, 1980; Vol. 42−3.

(4) (a) Kanaoka, Y.; Migita, Y.; Sato, Y.; Nakai, H. *Heterocycles* **1974**, *2*, 621. Sato, Y.; Nakai, H.; Wada, M.; Ogiwara, H.; Mizoguchi, T.; Migita, Y.; Hatanaka, Y.; Kanaoka, Y. *Chem. Pharm. Bull.* **1982**, *30*, 1639. (b) Sato, Y.; Nakai, H.; Ogiwara, H.; Mizoguchi, T.; Migita, Y.; Kanaoka, Y. *Tetrahedron Lett.* **1973**, 4565. (c) Kanaoka, Y.; Nagasawa, C.; Nakai, H.; Sato, Y.; Ogiwara, H.; Mizoguchi, T. *Heterocycles* **1975**, *3*, 553. (d) Yoon, U. C.; Kim, H. J.; Mariano, P. S. *Heterocycles* **1989**, *29*, 1041. Yoon, U. C.; Cho, S. J.; Oh, J. H.; Lee, L. G.; Kang, K. T.; Mariano, P. S. *Bull. Korean Chem. Soc.* **1981**, *12(3)*, 241. Yoon, U. C.; Oh, J. H.; Lee, S. J.; Kim, D. U.; Lee, J. G.; Kang, K. T.; Mariano, P. S. *Ibid.* **1992**, *13* (2), 166.

(5) (a) Maruyama, K.; Kubo, Y. *Chem. Lett.* **1978**, 769. (b) Mazzocchi, P. H.; Minamikawa, S.; Wilson, P. *J. Org. Chem.* **1979**, *44*, 1186.

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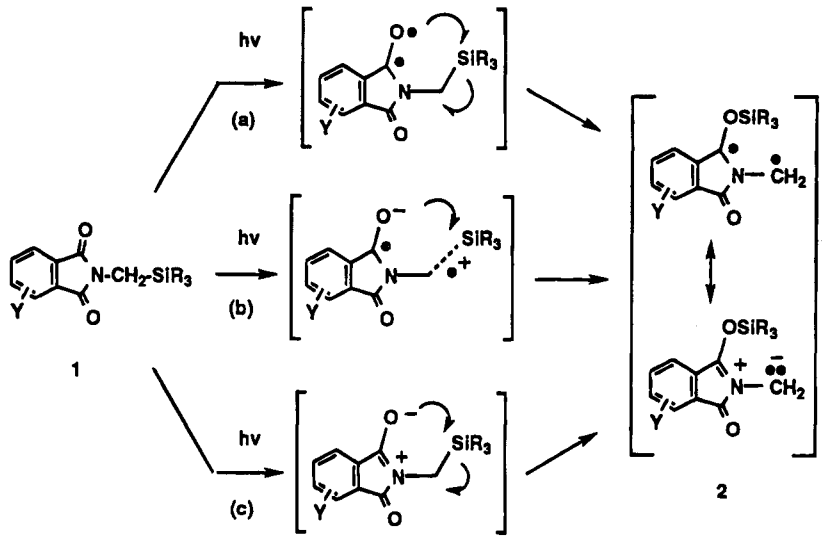
Scheme 1

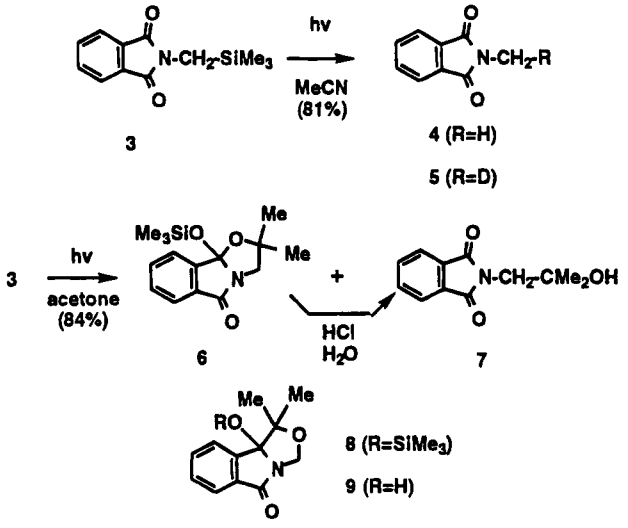


clear that alkylsilanes undergo photoaddition reactions with electron acceptors (*e.g.*, polycyanoarenes) which are driven by SET from σ_{C-Si} bonds.[6] In recent studies[7] we have observed reactivity of this type in tethered alkylsilane–phthalimide systems. The second issue relates to the reactivity of alkylsilanes with oxy radicals. The large σ_{O-Si} *vs* σ_{C-Si} bond energy difference appears to facilitate processes in which an alkylsilane TMS group is transferred to an oxy radical with concomitant homolytic cleavage of a C–Si bond (*i.e.*, S_H2 reactions).[8] Finally, the enhanced C–N π-bond order in phthalimide singlet excited states, which is presumably responsible for the observed cycloaddition reactivity of these substances, suggests that these excited species have zwitterionic character with negative and positive charge densities at the respective oxygen and nitrogen centers. This electronic profile suggests that excited phthalimides might be able to participate in polar type reactions such as those involving proton and silyl cation transfers.

A cumulative evaluation of these properties led us to predict that *N*-(silylmethyl)phthalimides **1** might display unique and interesting photochemical reactivity. Accordingly, we anticipated that excited states of these substances could react to produce novel azomethine ylides **2** by pathways involving either (1) TMS-group abstractions by an oxy-radical-like excited carbonyl (path a, Scheme 1), (2) sequential σ_{C-Si} to $\pi_{C=O}$ SET followed by TMS transfer (path b, Scheme 1), or (3) allowed-suprafacial sigmatropic silyl migration in a zwitterionic excited state (path c, Scheme 1). Below, we describe (1) investigations designed to evaluate this proposal, (2) observations that point out its validity, and (3) studies that probe a variety of interesting features of this novel azomethine ylide forming photochemical process. In addition, we report the results of studies exploring related photochemical reactions of *N*-phthaloyl-α-amino acid and 2-amino-1-phenylethanol derivatives.

Results

Photochemistry of *N*-[(Trimethylsilyl)methyl]phthalimide (3). Our exploratory efforts began with a study of the photochemical properties of the (silylmethyl)phthalimide **3**. Initially, a deceivingly simple observation was made. Specifically, irradiation (Pyrex) of this substance in deoxygenated MeCN leads to efficient (81%) production of the *N*-methyl analog **4**. Information about the mechanistic nature of this process came from a study of the photoreactions of **3** in D_2O–CH_3CN and H_2O–CD_3CN solutions. In the former case, the d_1-methylphthalimide (**5**) is generated, whereas all-protio **4** is formed in the latter reaction. In addition, irradiation of **3** in acetone leads to exclusive production of the solvent incorporation products **6** and **7**. The phthalimide alcohol **7** was shown to arise in this process by reaction of the photoadduct **6** during purification on silica. Likewise, **6** is converted to **7** upon treatment with HCl–H_2O at 25 °C.



The latter observations support the regiochemical assignment to **6** (*i.e.*, **6** and not **8**), which is also consistent with ^{1}H- and ^{13}C-NMR data. For example, the quaternary α-amide, quaternary α-oxa, and methylene carbons in the oxazolidine ring of **6** resonate at 113.9, 88.3, and 53.1 ppm, respectively. These shifts are more in accord with those expected for regioisomer **6** than **8** as is attested to by the fact that the related carbons in the known[4a] and closely related cyclic aminol **9** resonate at 95.9, 82.4, and 74.1 ppm. The final preliminary observation which demonstrates the unique nature of the (silylmethyl)phthalide **3** photoreaction is that extensive irradiation of *N*-methylphthalimide (**4**) in acetone fails to promote formation of adducts related to **6** (H instead of TMS), **7**, or **9**.

(6) Kyushin, S.; Masuda, Y.; Matsushita, K.; Nakadaira, Y.; Ohashi, M. *Tetrahedron Lett.* **1990**, *31*, 6395.

(7) Lee, Y. J.; Lee, C. P.; Jeon, Y. T.; Mariano, P. S.; Yoon, U. C.; Kim, D. U.; Kim, J. C.; Lee, J. G. *Tetrahedron Lett.* **1993**, *34*, 5855.

(8) See, for example: (a) Ingold, K. U.; Roberts, B. P. *Free Radical Substitution Reactions*; Wiley: New York, 1971. (b) Razuvaeu, G. A.; Vasileiskaya, N. S.; Muslin, D. V. *J. Organomet. Chem.* **1967**, *7*, 531. (c) Brook, A. G.; Ruff, J. M. *J. Am. Chem. Soc.* **1967**, *89*, 454. (d) Sakamoto, K.; Sakurai, H. *J. Am. Chem. Soc.* **1991**, *113*, 1466. Alberti, A.; Dellante, S.; Paradisi, C.; Roffia, S.; Pedulli, G. F. *J. Am. Chem. Soc.* **1990**, *112*, 1123.

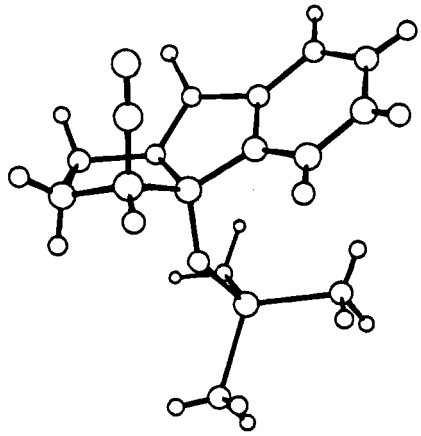
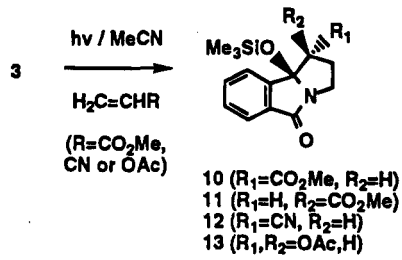


Figure 1. Chem-3D plot of X-ray crystallographic data obtained from analysis of the acrylonitrile–phthalimide cycloadduct **12**.

Our initial interpretation of the above results was that irradiation of **3** results in production of an azomethine ylide intermediate related to **2** (Y = H, Scheme 1). Cycloaddition of this intermediate with acetone as the dipolarophile would give **6**. In the absence of a trapping agent, reaction of the ylide with adventitious water would yield *N*-methylphthalimide.

Clear support for this proposal and information about the generality, mechanistic features, and synthetic utility of this process came from efforts probing other ylide-trapping reactions. Irradiation of (silylmethyl)phthalimide **3** in MeCN containing



0.09 M methyl acrylate leads to clean formation of the inseparable stereoisomeric adducts **10** and **11** (93%, 6:1 by ^{1}H-NMR). An identical reaction of **3** with acrylonitrile provides the related endo-adduct **12** (81%), exclusively. The regio- and stereochemical assignments of these substances were made on the basis of characteristic spectroscopic data as well as X-ray crystallographic analysis of **12** (Figure 1).

These results demonstrate that irradiation of (silylmethyl)-phthalimide **3** does indeed lead to clean generation of an azomethine ylide and that this intermediate is efficiently trapped in stereo- and regiochemically controlled dipolar cycloaddition reactions with electron deficient dipolarophiles. In contrast, trapping efficiencies are lower with electron rich dipolarophiles as reflected by the low-yielding generation of adduct **13** (20%) along with *N*-methylphthalimide (34%) from irradiation of an MeCN solution of **3** containing 0.09 M vinyl acetate.

Dipolarophile concentration appears to be an important factor in governing the quantum efficiencies of this ylide-forming photoreaction. This is seen qualitatively in the photoreactions of **3** in acetone solutions containing variable methyl acrylate concentrations. As methyl acrylate concentration decreases from 80 to 0.8 mM, the conversion of **3** to the acrylate and acetone adducts, **6** and **10** + **11**, increases and, as expected, the ratio of (**10** + **11**)/**6** decreases. Thus, methyl acrylate and likely other dipolarophiles quench the phthalimide excited state(s) which precede ylide formation. Consistent with this proposal are the results of quantum efficiency measurements. The quantum yields determined for formation of **10** + **11** are 4.2×10^{-3} and

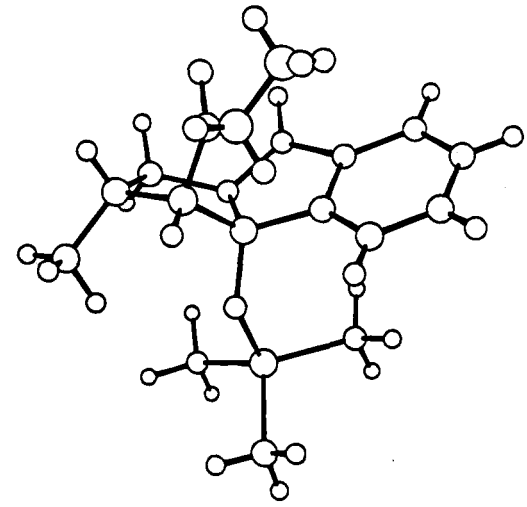
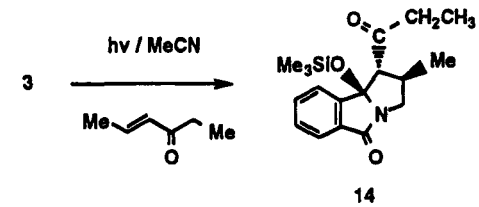


Figure 2. Chem-3D plot of X-ray crystallographic data obtained from analysis of the *trans*-hex-4-en-3-one silylphthalimide photoadduct **14**.

5.4×10^{-3} at methyl acrylate concentrations of 86 and 43 mM, respectively. Despite this, the highest chemical yields for adduct formation are obtained by using dipolarophile concentrations in the range of 100 mM. Also, the photoreactions occurring in acetone are activated in part by triplet sensitization. Consistent with this proposal is the observation that the photoprocess leading from **3** to **10** and **11** can be triplet sensitized by using acetophenone.

In order to further probe the stereochemical features of the ylide-trapping reaction, the photochemical reactions of silylphthalimide **3** with geometrically defined olefinic dipolarophiles were studied. Irradiation of **3** in an MeCN solution



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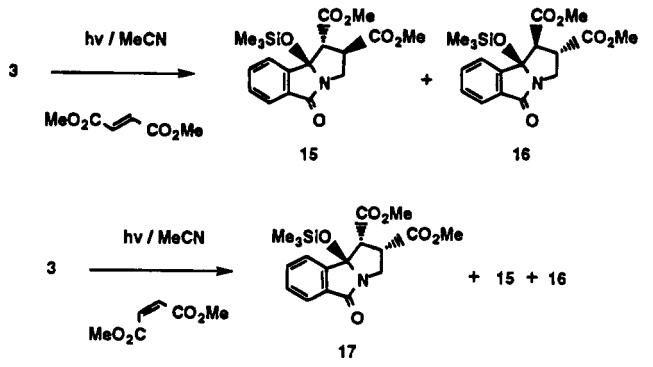
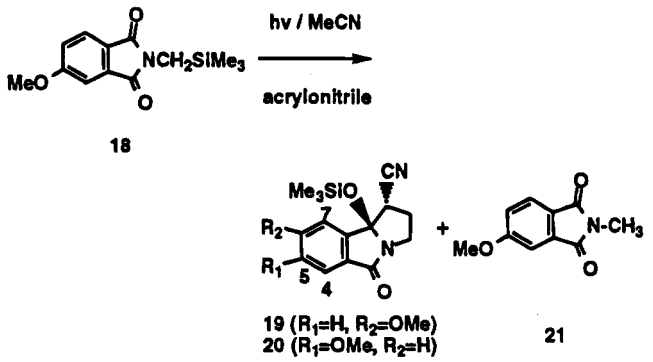
containing *trans*-hex-4-en-3-one (0.09 M) leads to the exclusive production of the adduct **14** in an isolated (silica chromatography) yield of 62%. X-ray crystallographic analysis of this substance (Figure 2) showed that it has the trans,trans stereochemistry at its three contiguous chiral centers in the pyrrolidine ring. In addition, the separable (47% and 24%, respectively) stereoisomeric adducts **15** and **16**, with trans relationships between the vicinal diester functions, are formed when an acetone solution of **3** containing dimethyl fumarate is irradiated. The photoreaction of **3** with dimethyl maleate is more complicated in that the ratio of the stereoisomeric products formed varies with the irradiation time/extent of conversion. A preparative reaction conducted at 80% conversion of **3** in acetone leads to the isolation (silica gel chromatography) of the trans,cis-adduct **17** (58%), trans,trans-adduct **15** (16%), and cis,trans-adduct **16** (15%). Under these conditions, dipolarophile cis–trans isomerization occurs to a small extent to give a 1:9 final ratio of the fumarate and maleate esters. However, ^{1}H-NMR analysis of the photolysate produced by low-conversion (*ca.* 10%) irradiation demonstrates that **17** is the sole primary product formed in the photoreaction of **3** with dimethyl maleate. Thus, **15** and **16** must arise in the maleate process by secondary epimerization reactions of **17**. The stereochemical assignments to the adducts formed in the fumarate and maleate ester photoreactions with **3** were made on the basis of their



characteristic ^{1}H- and ^{13}C-NMR properties and comparisons made with the acrylate adducts **10** and **11** (see Experimental Section). The combined results show that the ylide-trapping reactions with dipolarophiles are both highly diastereoselective (endo preference) and stereospecific (retention of olefin stereochemistry).

The final question addressed in this study of (silylmethyl)-phthalimide photochemistry concerns the regiochemistry of the C to O silyl migration process and its control by aryl ring substituents. This issue was explored by use of the methoxy- and carbomethoxy-substituted phthalimides **18** and **22**, substances which are prepared from known[9] N−H precursors by silylmethylation. Irradiation of **18** in an MeCN solution

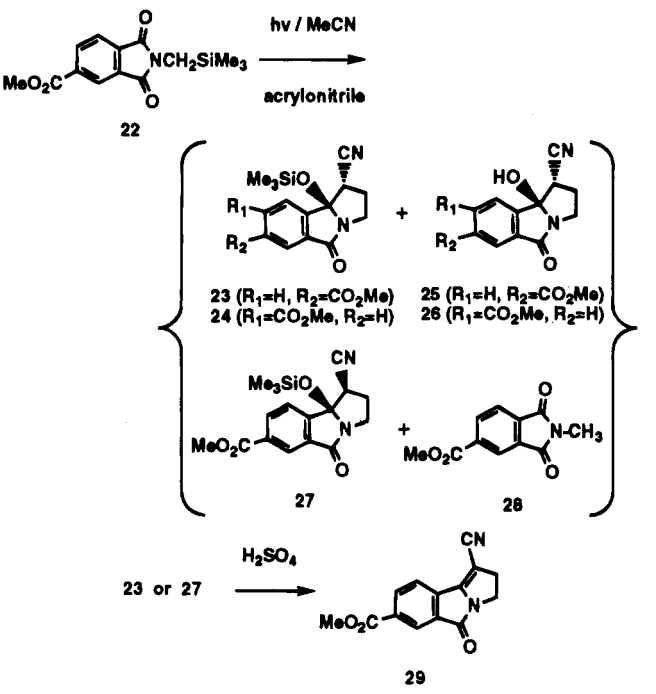


containing 0.09 M acrylonitrile leads to inefficient formation of a single adduct **19** (10% isolated, 21% by ^{1}H-NMR analysis) and the *N*-methylphthalimide **21** (7% isolated, 17% by ^{1}H-NMR). The regiochemical assignment to **19** (rather than **20**) was based on analysis of the ^{1}H-NMR pattern of resonances in the aromatic region (7.03 ppm, s, H-7; 7.04 ppm, d, H-5; 7.68 ppm, d, H-4; see Experimental Section).

More efficient but less selective is the photoreaction of the carbomethoxy analog **22** with acrylonitrile. In this case, a complex mixture of partially separable products **23**−**28** is produced. The yields for formation of these substances are as follows: isolated, **23** + **24** (21%), **25** + **26** (30%), **27** (1%), **28** (11%); ^{1}H-NMR analysis of crude photolysate, **23** (33%), **24** (34%), **25** + **26** (0%), **27** (11%), **28** (20%). The regiochemical and stereochemical assignments to these substances were aided by their spectroscopic properties and comparisons of these between members of this series and with related adducts (see above). Also, the epimeric relationship of **23** and **27** is proven by the observation that both substances can be converted to the same unsaturated product, **29**, by treatment with concentrated sulfuric acid.

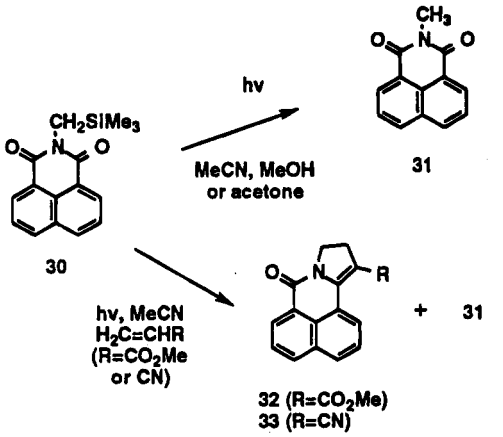
The results show that photoreaction of the methoxysilylphthalimide **18** occurs by exclusive C to O silyl migration

(9) Mazzocchi, P. H.; Wilson, P.; Khachik, F.; Klinger, L.; Minamikawa, S. *J. Org. Chem.* **1983**, *48*, 2981.



to the carbonyl group meta to the electron-donating MeO substituent. In contrast, silyl migration in the carbomethoxy-substituted phthalimide is unselective, giving nearly equal quantities of the regioisomeric ylides.

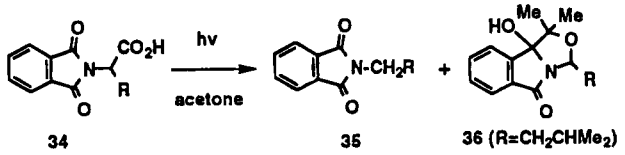
Photochemistry of *N*-[(Trimethylsilyl)methyl]-1,8-naphthalimide (30). With the intent of delineating the generality of this novel silyl migration reaction, we have investigated the excited state chemistry of the silylnaphthalimide **30**. Qualita-



tively similar but quantitatively different results have come from this effort. For example, as for the phthalimide **3**, irradiation of MeCN or MeOH solutions of **30** leads to efficient production of the *N*-methyl analog **31**. But in contrast with **3**, only **31** is generated even when an acetone solution of **30** is irradiated. Similarly, the ylide derived by irradiation of **30** is only poorly trapped by methyl acrylate and acrylonitrile, as is indicated by the low yields of the respective adducts **32** (17%) and **33** (18%) and the high yields (49% and 50%, respectively) of the *N*-methylnaphthalimide **31** that are formed. Finally, the initially formed dipolar cycloaddition products undergo rapid elimination while those arising from the phthalimide **3** do not.

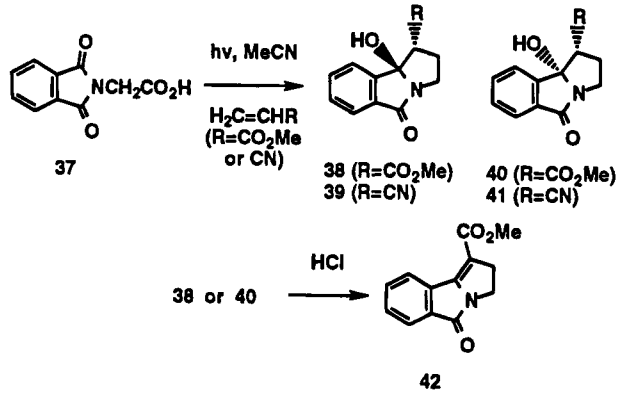
Photochemistry of *N*-Phthaloylglycine, -alanine, -phenylalanine, and -2-amino-1-phenylethanol. Within the results

of an earlier study by Kanaoka and his co-workers[10] is found the suggestion that α-phthalimidoacetic acid derivatives undergo ylide-forming photoreactions, similar to the process described above. For example, Kanaoka observed that irradiation of a variety of substances of type **34**, originating from naturally

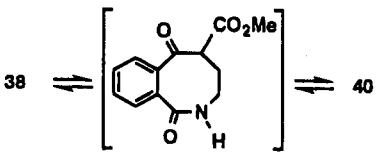


occurring α-amino acids, in acetone results in efficient formation of the decarboxylation products **35**. However, in one case, that of *N*-phthaloylleucine (**34**, R = CH_2CHMe_2), the adduct **36** was reported to be produced as a minor (2%) product.

To determine if *N*-phthaloyl-α-amino acids do indeed undergo efficient formation of azomethine ylides upon irradiation, the photochemistry of the glycine derivative **37** was explored. Irradiation of **37** in MeCN solutions containing the dipolaro-



philes methyl acrylate and acrylonitrile, as anticipated, does lead to production of the respective, separable pairs of adducts **38** + **40** (39%) and **39** + **41** (86%). ^{1}H- and ^{13}C-NMR analysis shows that these amidols exist as non-rapidly interconverting epimers to which we have assigned the respective trans and cis relative configurations based on comparisons of the spectroscopic data with those of their nonepimerizable OTMS analogs **10**–**12**. Moreover, the stereoisomeric relationship between **38** and **40** is documented by the independent conversion of both substances to the unsaturated benzopyrrolizidine **42** *via* treatment with dilute hydrochloric acid. Also, **38** and **40** each equilibrate to form an *ca.* 1:1 mixture of both on standing in $CDCl_3$ solutions for extended time periods (*ca.* 24 h). This equilibrium most likely occurs by reversible ring opening through the azocinedione intermediate **43**.



Information about stereochemical preferences at yet another potentially chiral center formed in the ylide photogeneration–cycloaddition sequence has come from studies with the L-alanine- and L-phenylalanine-derived phthalimides, **44** and **50**. Irradiation of the alanine derivative **44** in an MeCN solution containing methyl acrylate leads to generation of a complex

(10) Sato, Y.; Nakai, H.; Mizoguchi, T.; Kawanishi, M.; Kanaoka, Y. *Chem. Pharm. Bull.* **1982**, *30*, 1263.

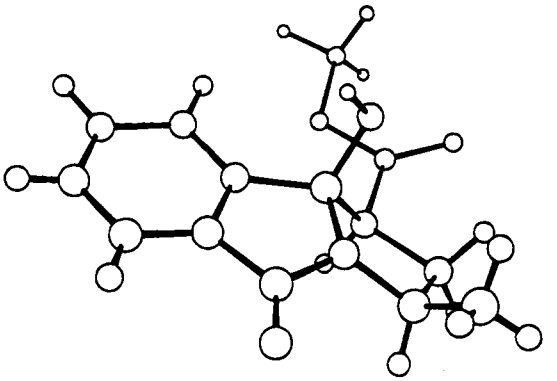
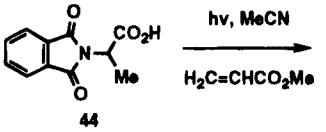
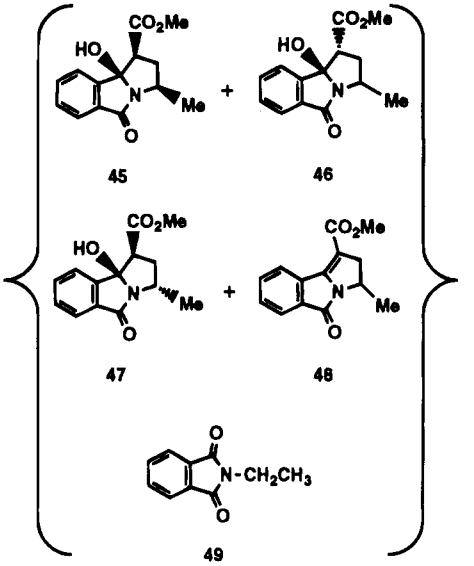


Figure 3. Chem-3D plot of X-ray crystallographic data obtained from analysis of the methyl acrylate–phthaloylalanine photoadduct **45**.





mixture of products whose composition varies with irradiation times. Silica gel chromatographic separation of this mixture leads to isolation of the adducts **45** (18%), **46** (42%), and **47** (trace), the dehydration product **48** (9%), and *N*-ethylphthalimide **49** (9%). TLC and ^{1}H-NMR monitoring of the progress of this photoreaction reveals that **46** is the sole and initial adduct formed and that with time it slowly undergoes a dark isomerization to yield the other adducts, **45** and **47**, and dehydration to produce **48**. Owing to the isomerization and dehydration processes, it is difficult to obtain absolutely pure samples of **46** and **47**. However, adduct **45** can be isolated in pure form as a crystalline substance. Consequently the relative stereochemistry at the three chiral centers in **45** can be confidently assigned by X-ray crystallographic methods (Figure 3). The ^{1}H-NMR spectroscopic data accumulated for **45** and **47** (see below) show that these substances have the same cis relationship between the C_5-OH and C_6-CO_2Me centers. Thus, **47** must be the the C_7-epimer of **45**. A similar analysis of the spectroscopic properties of **46** shows that it has the trans relative stereochemistry at C_5–C_6, but unfortunately, it fails to reveal information for stereochemical assignment of the C_7-methyl substituent.

In a similar manner, the phenylalanine derivative **50** is transformed to a mixture of products when it is subjected to

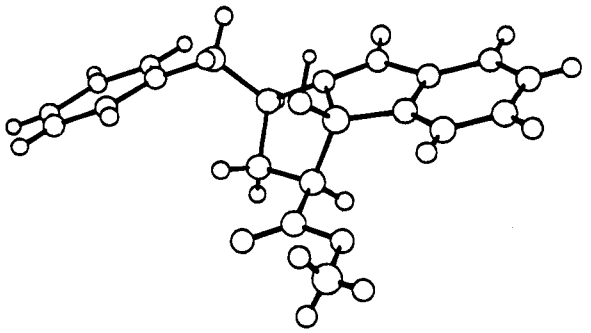
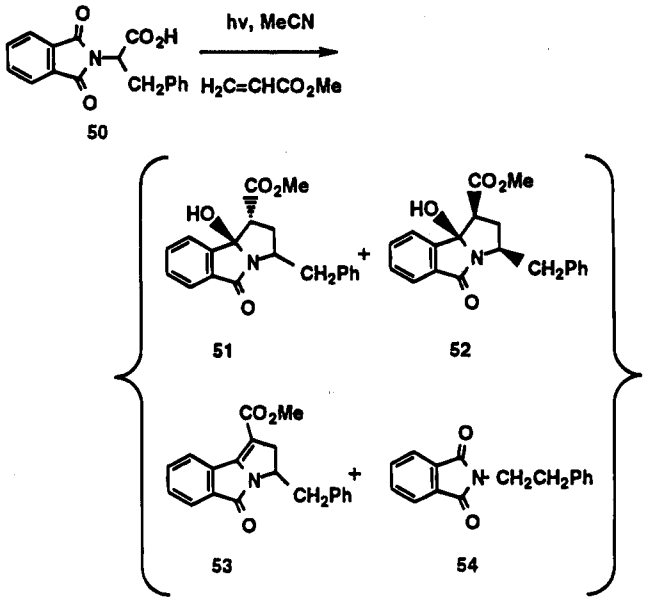


Figure 4. Chem-3D plot of X-ray crystallographic data obtained from analysis of the methyl acrylate–phthaloylphenylalanine photoadduct **52**.

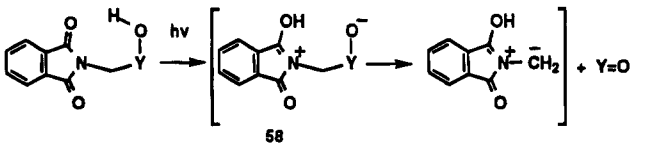
these irradiation and chromatographic conditions. Specifically, photolysis of **50** in the presence of methyl acrylate leads to isolation of the adducts **51** (38%), **52** (17%), the unsaturated ester **53** (7%), and *N*-phenethylphthalimide **54** (14%). Here



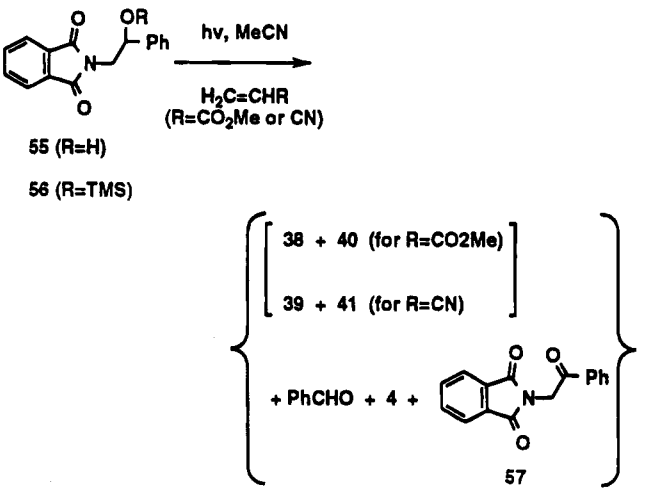
again, ^{1}H-NMR and TLC monitoring of the photolysate at low conversion show that **51** is the sole primary photoproduct and that it is transformed to **52** and **53** by dark processes. While the C_5,C_6,C_7 stereochemistry of **52** is easily assigned as cis,cis based on its X-ray crystallographic properties (Figure 4), that of the primary photoadduct **51** is not. ^{1}H-NMR spectroscopic data for **51** and **52** indicate that these substances possess the opposite C_5–C_6 relative stereochemistry. Thus, **51** has the trans hydroxyl ester stereochemistry. This analysis, used in a number of instances above, is exemplified by the chemical shifts of the methyl ester protons which for the trans isomers with endo ester dispositions are consistently located upfield of those for the cis exo ester isomers. Examples of these phenomena are found in **38**, **46**, and **51**, where the OMe protons resonate in the 3.1–3.2 ppm region, while in **40**, **45**, **47**, and **52** they appear between 3.8–3.9 ppm. Accordingly, **51** has a trans relationship between the hydroxyl and carbomethoxy groups, but its relative stereochemistry at C_7 cannot be assigned on the basis of the information which is currently available.

The final system studied in this effort is the phthalimidoethanol derivative **55**. Although the side chain present in **55** is unlike that of the silylmethyl and acetic acid analogs, this

Scheme 2



substance also participates in an ylide-forming photoreaction.[11] Irradiation of **55** in an acetone solution containing methyl



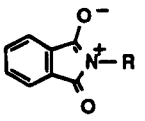
acrylate (0.2 M) results in production of the epimeric adducts **38** (26%) and **40** (7%) along with lesser quantities of the *N*-phenacylphthalimide **57** (4%), *N*-methylphthalimide **4** (7%), and benzaldehyde. Similarly, photoreaction of **55** in acetone with acrylonitrile yields the adducts **39** (6%) and **41** (9%) together with **4** (5%), **57** (6%), and benzaldehyde. Two additional observations are informative. Firstly, irradiation of the phthalimide alcohol **55** in acetone or acetonitrile in the absence of an added dipolarophile leads to production of the methylphthalimide **4** (37%), phenacyl derivative **57** (4%), and benzaldehyde (60%). Secondly, in contrast the OTMS analog **56** is unreactive when irradiated in acetone or acetonitrile solutions for comparable time periods.

Discussion

Mechanism(s) for Azomethine Ylide Formation. The photochemical transformations of the (silylmethyl)phthalimides and related acetic acid and phenylethanol derivatives to azomethine ylide intermediates described above share a common feature. Specifically, in these excited state processes an electrofugal group (H^+ or Me_3Si^+) is transferred to a carbonyl oxygen of the excited phthalimide chromophore. In the TMS system, this leads directly to an ylide if the process occurs in the singlet manifold. A diradical precursor of this ylide would be generated from the triplet phthalimide excited state (Scheme 1). Evidence gained from acetone and acetophenone sensitization studies shows that triplet phthalimides do undergo the C to O silyl transfer process. However, we have not yet assigned multiplicities to the reactive excited states in the direct irradiation processes. In contrast, proton transfer in the reactions of the phthalimidoacetic acid and phenylethanol derivatives results in generation of the charged separated intermediates **58** (Scheme 2). Thermodynamically driven carbon–carbon bond fragmentation in these species leads to simultaneous formation of carbonyl (CO_2 or PhCHO) products and the azomethine ylide intermediate.

(11) McCormac, P.; Pratt, A. *Abstracts*, XVth IUPAC Symposium on Photochemistry, Prague, Czech Republic, 1994; p 111.

The electronic properties of the phthalimide excited state(s) facilitate the key electrofugal group transfer processes. The known propensity of phthalimide singlets to enter into 2 + 2 cycloaddition chemistry with olefins[5] indicates that these species have zwitterionic character (*e.g.*, **59**) with large C−N π-bond



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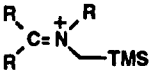

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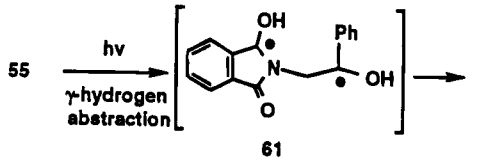
orders and high positive and negative charge densities located at the respective nitrogen and oxygen centers. This electronic distribution could foster ylide formation. Indeed, *N*-(trimethylsilyl)methyliminium cations (*e.g.*, **60**) are known[12] to rapidly react to produce azomethine ylides by transfer of the silyl moiety to nucleophiles. In addition, zwitterionic, phthalimide singlets have a basic oxygen center which could induce C to O silyl transfer and deprotonation reactions (Scheme 2) at tethered carboxylic acid and alcohol sites.

In contrast, triplet excited states of phthalimides, like their ketone analogs, display oxy-radical-like rather than oxy-anion-like reactivity. These transients typically participate in Norrish type-II hydrogen atom abstraction chemistry. Indeed, we have already shown[7] that oxy-radical-like, triplet carbonyls do not undergo analogous TMS abstraction processes, even in those cases where the processes can proceed *via* six-membered transition states. Thus, it is unlikely that ylide formation in the excited state chemistry of the (silylmethyl)phthalimides is promoted by radical abstraction of a β-TMS group (*i.e.*, *via* a five-membered transition state). Likewise, Norrish type-II reaction of the phthalimidophenylethanol **55** would likely favor γ-benzylic H-atom abstraction and produce the diradical **61**. No reasonable pathway exists to transform **61** to the observed azomethine ylide. Rather, fragmentation to generate the phthalimide and acetophenone enol pair would be a more reasonable, yet nonobserved, reaction of **61**.



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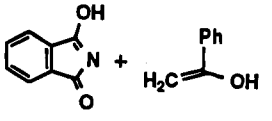
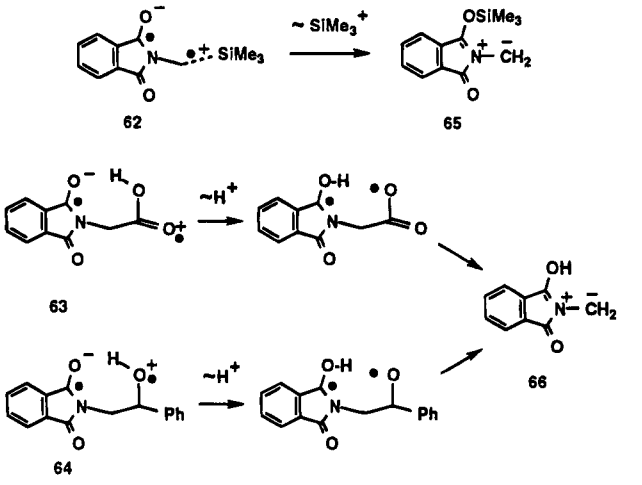
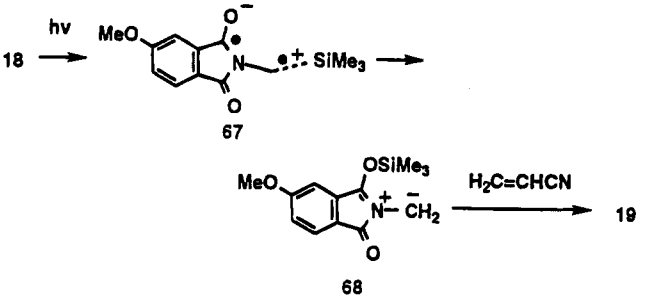


The final and perhaps most reasonable mode for activation of ylide formation in both the triplet and singlet excited state reactions of the phthalimide derivatives is charge or electron transfer. It has been long recognized[5] that electronic excited states of phthalimides are good electron acceptors. Furthermore, alkylsilanes,[6] carboxylic acids, and alcohols all are documented to serve as electron donors in photoinduced SET processes.[13] Charge or electron transfer in the phthalimido silanes, acids, and alcohols would produce charge-separated diradicals **62**−**64**, transients with proper electronic features necessary to drive ylide formation (*i.e.*, to induce transfer of an electrofugal group from carbon to oxygen) (Scheme 3).

Scheme 3



The high regioselectivity observed for TMS migration in the excited state chemistry of the methoxy-substituted (silylmethyl)-phthalimide **18** may be consistent with the view that these processes are driven by the electron-accepting natures of phthalimide excited states. Accordingly, carbonyl anion radical localization meta to the electron-donating methoxy substituent (as in **67**) may be the reason why ylide **68** is produced solely in the photoreaction of **18**. While this argument serves to



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rationalize the results and to support the SET mechanistic proposals, it requires a firm theoretical base and additional testing. In this regard, the lack of regiocontrol seen in photoreaction of the carbomethoxy analog **22** is a questionable feature of these interpretations. It is clear that, while these excited state transformations are novel, synthetically interesting, and potentially general,[14] they require further study to more fully understand their mechanistic characteristics.

Cycloaddition Chemistry. The synthetic potential of the novel photochemical processes described above derives from the facts that azomethine ylides are the primary photoproducts and that these dipolar reactive intermediates can be readily trapped in concerted 4 + 2 cycloaddition reactions with a variety of dipolarophiles.[15] As a result, the overall sequences, consisting of photoinduced ylide formation and dipolar cycloaddition, serve to generate structurally complex and highly functionalized N-heterocyclic products containing the pyrrolizidine ring skeleton. Moreover, the reactions are high yielding, and they occur with high degrees of regiochemical and stereochemical control.

The regiochemical outcome of the cycloaddition processes of the photogenerated azomethine ylides **65** and **66** (Scheme 3) are governed by electronic factors. For example, reactions of

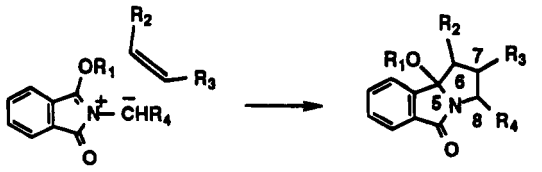
(12) Padwa, A.; Haffmans, G.; Tomas, M. *Tetrahedron Lett.* **1983**, *24*, 4303. Vedejs, E.; Martinez, G. R. *J. Am. Chem. Soc.* **1979**, *101*, 6452.

(13) Mariano, P. S.; Stavinoha, J. *Synthetic Organic Photochemistry*; Horspool, W. M., Ed.; Plenum Press: New York, 1984.

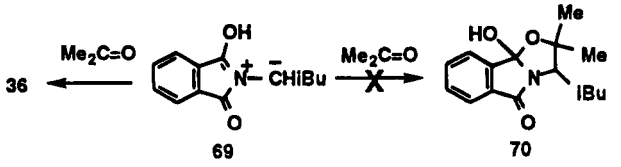
(14) We have recently shown that azomethine ylide forming, C to O silyl transfer processes operate in the photochemistry of conjugated cyclic and acyclic (silylmethyl)imides (Yoon, U. C.; Cho, S. J.; Lee, Y. J.; Mariano, P. S. Unpublished work).

(15) Deyrup, J. A. *Small Ring Heterocycles*; Hassner, A., Ed.; Wiley: New York, 1983; p 131.

Scheme 4



65 and **66** with electron withdrawing group substituted olefins such as acrylonitrile are highly regioselective. These results are consistent with FMO considerations[16] and with the view that the HOMOs of these 4π-electron systems have high coefficients at the exocyclic methylene carbons. The consequences of this are seen also in the reaction of ylide **65** with acetone where the adduct **6**, resulting from bonding between the ylide exocyclic methylene carbon and the carbonyl carbon of the ketone, is formed exclusively. This result should be compared to an earlier isolated observation by Kanaoka[10] that a related ylide **69**, derived from *N*-phthaloylleucine **34**, reacts



with acetone to give adduct **36**. Although **36** was formed in only a 2% yield (thus, its regioisomer might not have been detected), the differences in the regiochemical course of the two processes might be a consequence of steric effects. Accordingly, formation of the electronically preferred regioisomer **70** by reaction of **69** with acetone would be disfavored owing to the repulsive interactions developing between the *gem*-dimethyl and vicinal isobutyl groups.

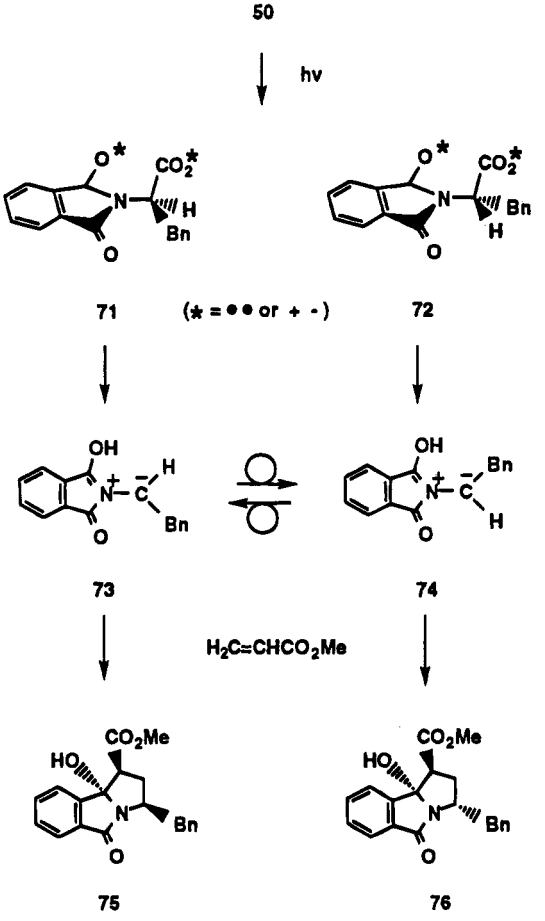
The high degrees of stereoselectivity, stereospecificity, and regioselectivity observed for the dipolar cycloaddition reactions of ylides **65** and **66** heighten the overall synthetic interest in these new photochemical processes. In general, the trapping reactions of ylides related to **65** and **66** can lead to the generation of four contiguous chiral centers (C_5–C_8) in the forming pyrrolizidine ring system (Scheme 4). The C_5–C_6 relative stereochemistry in these processes appears to be strongly governed by the electronically driven preference for endo-cycloaddition transition states. This is exemplified by reaction of ylide **65** with acrylonitrile and dimethyl maleate which yields the respective endo-adducts **12** and **17** exclusively.

The relative stereochemistry established at the C_6 and C_7 centers is determined by dipolarophile stereochemistry since, as expected, these processes occur with retention of olefin stereochemistry. The stereospecificity is exemplified by the formation of adducts **17** and **15** + **16** in reaction of (silylmethyl)-phthalimide **3** with the maleate and fumarate esters.

The final chiral center which can be installed by these cycloaddition reactions originates from the phthalimide exocyclic alkyl substituent and is located at C_8 in the pyrrolizidine skeleton (Scheme 4). The degree of stereochemical control in the creation of this chiral center appears to be quite high as demonstrated by the exclusive production of adduct **51** from photoreaction of *N*-phthaloylphenylalanine **50** with methyl acrylate. Yet the reasons for this selectivity are difficult to assign. Two ylides stereoisomers/conformers can be produced

(16) (a) Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; Wiley: New York, 1976. (b) Houk, K. N.; Sims, J.; Watts, C. R.; Luskus, L. J. *J. Am. Chem. Soc.* **1973**, *95*, 7301. (c) Houk, K. N. *Pericyclic Reactions*; Marchand, A. P., Lehr, R. E., Eds.; Academic Press: New York, 1977; Vol. 2.

Scheme 5



in the photoinduced decarboxylation of **50**, one having the *E*-exocyclic C=N bond stereochemistry (**73**) and the other with *Z*-stereochemistry (**74**) (Scheme 5). If these ylide stereoisomers interconvert by C–N bond rotation or reversible aziridine ring formation more slowly than they react with the dipolarophile, the production of a single stereoisomeric adduct would suggest that one ylide isomer is more rapidly generated in the photodecarboxylation process and subsequently trapped by an endo cycloaddition with methyl acrylate. Rationalization for a kinetic preference for formation of one of the two ylide isomers **73** or **74** would need to invoke a conformational bias favoring one of the decarboxylation transition states related to **71** or **73**. The factors governing this type of selectivity are not obvious. Alternatively, the ylide stereoisomers **73** and **74** could be in rapid equilibrium. In this event, exclusive formation of one stereoisomeric adduct would imply that one of the ylide isomers undergoes cycloaddition more rapidly. Here again, it is not obvious why this kind of kinetic preference would exist.

The observations described and discussed above demonstrate that our photochemical studies with *N*-(silylmethyl)phthalimides and related acetic acid and phenylethanol derivatives have uncovered new and synthetically useful chemistry. While several mechanistic questions remain unanswered, we already know[14] that azomethine ylide photogeneration by use of the methodology outlined above can be extended to other imide systems. Our continuing efforts are aimed at delineating the mechanistic features, generality, and synthetic potential of this chemistry.

Experimental Section

General. NMR spectra are recorded on $CDCl_3$ solutions unless otherwise noted. Chemical shifts are reported in parts per million (ppm) relative to $SiMe_4$ or $CHCl_3$ as internal standards. ^{13}C-NMR assignments

are aided by INEPT or DEPT results for determining the number of attached hydrogens. Infrared spectral bands are reported in wavenumbers (cm^{-1}). Mass spectra (MS or HRMS) were recorded using electron impact ionization unless specified as chemical ionization (CI). All compounds were obtained as oils (unless specified otherwise by giving recorded melting points) and in purities of >90% as judged by ^{1}H- and ^{13}C-NMR. All preparative irradiations were conducted by using an immersion apparatus (Hanovia 450 W, medium-pressure lamp) at a solution temperature of *ca.* 20 °C and using cutoff filters (Vycor λ > 220 nm, Pyrex λ > 290 nm and uranium λ > 320 nm). *N*-[(Trimethylsilyl)methyl]phthalimide (Petrarch), 1,8-naphthalimide (Aldrich), chlorotrimethylsilane (Petrarch), acrylonitrile (Aldrich), methyl acrylate (Aldrich), dimethyl maleate (Aldrich), dimethyl fumarate (Aldrich), and *trans*-4-hexen-3-one (Aldrich) are commercial materials.

Photochemistry of *N*-[(Trimethylsilyl)methyl]phthalimide (3). In MeCN. A solution of (silylmethyl)phthalimide **3** (500 mg, 2.14 mmol) in 200 mL of MeCN was irradiated in a preparative apparatus with Pyrex-filtered light under N_2 for 24 h (100% conversion of **3**). Concentration of the photolysate gave a residue, which was subjected to chromatography (silica, 1:4 EtOAc−hexane) yielding 279 mg (81%) of *N*-methylphthalimide (**4**).

In CD_3CN-H_2O and CH_3CN-D_2O. Two solutions containing **3** (3 mg, 0.015 mmol) in 0.6 mL of either CD_3CN-H_2O (12:1) or CH_3CN-D_2O (1:1) were irradiated for 17 h (100% conversion of **3**). ^{1}H-NMR analysis of the photolysates showed that *N*-methylphthalimide (**4**) was formed in the CD_3CN-H_2O reaction while its *N*-CDH_2 (^{1}H-NMR 3.15 (t, J = 2.0 Hz, 2 H, CH_2D)) analog **5** was obtained in the CH_3CN-D_2O reaction.

In Acetone. A solution of **3** (500 mg, 2.14 mmol) in 200 mL of acetone was irradiated for 3 h (100% conversion of **3**) and subjected to workup and purification as described above, giving 421 mg (67%) of the acetone adduct **6** and 75 mg (16%) of the phthalimido alcohol **7** (mp 101−102 °C).

6: ^{1}H-NMR −0.09 (s, 9 H, $SiMe_3$), 1.03 (s, 3 H, Me_2), 1.52 (s, 3 H, Me_2), 3.22 (d, J = 11.3 Hz, 1 H, NCH_2), 3.90 (d, J = 11.3 Hz, 1 H, NCH_2), 7.43−7.70 (m, 4 H, aromatic); ^{13}C-NMR 0.6 ($SiMe_3$), 28.2 (Me_2), 53.1 (NCH_2), 88.3 (OC), 122.1, 123.8, 130.2, 130.7, 133.5, 146.1 (aromatic), 171.2 (C=O); IR 1702; MS *m/z* (relative intensity) 291 (m, 0.3), 276 (15), 232 (100), 218 (6), 202, (64), 160 (11), 148 (10), 130 (14); HRMS *m/z* 291.1291 ($C_{15}H_{21}NO_3Si$ requires 291.1291).

7: ^{1}H-NMR 1.21 (s, 6 H, Me_2), 2.67 (s, 1 H, OH), 3.70 (s, 2 H, NCH_2), 7.65−7.83 (m, 4 H, aromatic); ^{13}C-NMR 27.5 (Me_2), 49.2 (NCH_2), 71.5 (OC), 123.5, 131.9, 134.2 (aromatic), 169.3 (C=O); IR 3400 (br) 1699; MS (CI) *m/z* (relative intensity) 220 (M + 1, 2.4), 204 (14), 202 (25), 201 (19), 162 (23), 161 (100), 160 (53), 118 (3); HRMS *m/z* on M − H_2O 220.0973 ($C_{12}H_{14}NO_3$ requires 220.0974).

In MeCN Containing Methyl Acrylate. A solution of **3** (400 mg, 1.72 mmol) and methyl acrylate (1.47 g, 17.1 mmol) in 200 mL of MeCN was irradiated under the above conditions for 31 h (12% conversion of **3**). Workup and chromatography as described above gave 61 mg (93% based on recovered **3**) of adducts **10** and **11** as a 6:1 mixture of two diastereomers.

10 (major diastereomer): ^{1}H-NMR −0.17 ($SiMe_3$), 2.49 (m, 1 H, $-CH_2CH_2N$), 2.68 (m, 1 H, $-CH_2CH_2N$), 3.10 (OCH_3), 3.29 (d, 1 H, J = 7.1 Hz, $CHCO_2$), 3.40 (dd, 1 H, J = 9.5 and 9.5 Hz, CH_2N), 3.93 (dd, 1 H, J = 9.5 and 9.5 Hz, CH_2N), 7.43 (m, 1 H, aromatic), 7.50 (m, 2 H, aromatic), 7.64 (m, 1 H, aromatic); ^{13}C-NMR 0.6 ($SiMe_3$), 30.9 (CH_2), 42.0 (CH_2N), 51.3 (CH_3O), 53.0 (CH), 99.1 (COSi), 123.2, 123.4, 130.0, 132.3, 132.6, 144.5 (aromatic), 170.4 (C=O), 171.6 (C=O); MS *m/z* (relative intensity) 319 (m, 13), 304 (3), 288 (2), 260 (2), 232 (100), 230 (39), 198 (29), 178 (28); HRMS *m/z* 319.1240 ($C_{16}N_{21}NO_4Si$ requires 319.1240).

11 (minor diastereomer): ^{1}H-NMR 0.11 ($SiMe_3$), 2.49 (m, 1 H, CH_2), 2.69 (m, 1 H, CH_2), 3.96 (OCH_3), 3.33 (d, J = 8.8 Hz, 1 H, $CHCO_2$), 3.397 (dd, J = 9.8, 9.8 Hz, 1 H, CH_2N), 3.95 (dd, J = 9.8, 9.8 Hz, 1 H, CH_2N), 7.65 (m, 4 H, aromatic); ^{13}C-NMR 1.3 ($SiMe_3$), 33.9 (CH_2), 39.9 (CH_2N), 51.7 (OC), 123.3, 126.5, 131.3, 132.0 (aromatic), 170.4, 171.6 (C=O).

In MeCN Containing Acrylonitrile. Irradiation of **3** in MeCN (same molar equivalents as for the methyl acrylate reaction above) for 31 h (10% conversion of **3**) followed by workup and purification as described above gave 40 mg (81% based on recovered **3**) of the adduct **12** (mp 103−104 °C, EtOAc−hexane) as a single diastereomer: ^{1}H-NMR −0.15 (s, 9 H, $SiMe_3$), 2.60 (m, 1 H, CH_2), 2.88 (m, 1 H, CH_2), 3.37 (d, J = 6.8 Hz, 1 H, CHCN), 3.48 (dd, J = 9.7, 9.7 Hz, 1 H, CH_2N), 3.91 (ddd, J = 9.7, 9.7, 8.7 Hz, 1 H, CH_2N), 7.51−7.92 (m, 4 H, aromatic); ^{13}C-NMR 0.45 ($SiMe_3$), 32.4 (CH_2), 39.7 (CHCN), 41.0 (CH_2N), 98.1 (CO), 117.3 (CN), 123.0, 124.0, 130.9, 132.1, 133.3, 144.2 (aromatic), 170.0 (C=O); MS *m/z* (relative intensity) 286 (m, 26), 271 (34), 233 (91), 232 (100), 218 (8), 197 (39); HRMS *m/z* 286.1138 ($C_{15}H_{18}N_2O_2Si$ requires 286.1136).

In MeCN Containing Vinyl Acetate. A solution of **3** (400 mg, 1.71 mmol) and vinyl acetate (1.48 g, 17.1 mmol) in CH_3CN was irradiated for 4 h (85% conversion of **3**), worked up and purified as described above. This gave 92 mg (20%) of adduct **13** as a single diastereomer and 80 mg (34%) of *N*-methylphthalimide (**4**).

13: ^{1}H-NMR ($CDCl_3$) −0.19 (s, 9 H, $Si(CH_3)_3$), 1.39 (s, 3 H, $COCH_3$), 2.21−2.26 (m, 1 H, $CH(OCOCH_3)CH_2CH_2N$), 2.69−2.78, (m, 1 H, $CH(OCOCH_3)CH_2CH_2N$), 3.34−3.40 (m, 1 H, CH_2CH_2N), 3.73−3.80 (m, 1 H, CH_2CH_2N), 5.37 (d, 1 H, J = 4.12 Hz, $CH(O_2CCH_3)$), 7.40−7.50 (m, 3 H, aromatic), 7.63−7.65 (m, 1 H, aromatic); ^{13}C-NMR ($CDCl_3$) 0.6 ($Si(CH_3)_3$), 20.1 (O_2CCH_3), 32.7 ($CH(O_2CCH_3)CH_2CH_2N$), 40.6 (CH_2CH_2N), 75.2 ($-CH(O_2CCH_3)$), 99.4 (quaternary C-3), 123.0, 124.1, 129.8, and 132.2 (aromatic, CH), 133.4 and 143.7 (aromatic, C), 169.4 (imide C=O), 170.9 (ester C=O); IR (neat) 1710 (imide C=O), 1720 (ester C=O); MS *m/z* (relative intensity) 320 M^+ + 1, 20), 319 (M^+, 56), 304 (M^+ − CH_3, 8), 277 (100), 276 (M^+ − $COCH_3$, 1), 262 (25), 232 (87), 220 (16), 204 (39), 186 (25), 170 (29); HRMS *m/z* 319.1237 ($C_{16}H_{21}NO_4Si$ requires 319.1240).

In MeCN Containing *trans*-Hex-2-en-3-one. A solution of **3** in MeCN containing *trans*-hex-2-en-3-one (same molar equivalents as above) was irradiated for 8.5 h (40% conversion of **3**) worked up, and the residue was purified as described above. This gave 131 mg (60%) of the adduct **14** (mp 73.5−74.5 °C, EtOAc−hexane) as a single diastereomer: ^{1}H-NMR −0.19 (s, 9 H, $SiMe_3$), 0.61 and 0.62 (t, J = 7.2 Hz, 3 H, Me), 1.24 (d, J = 7.2 Hz, 3 H, Me), 2.19 (qd, J = 18.1, 7.2 Hz, 1 H, CH_2), 2.38 (qd, J = 18.1, 7.2 Hz, 1 H, CH_2), 2.71 (m, 1 H, CH), 2.95 (dd, J = 11.5, 5.8 Hz, 1 H, CH_2N), 3.28 (d, J = 3.9 Hz, 1 H, CHCO), 4.20 (dd, J = 11.5, 8.3 Hz, 1 H, CH_2N), 7.35−7.66 (m, 4 H, aromatic); ^{13}C-NMR 0.9 ($SiMe_3$), 7.0 (CH_3), 20.2 (CH_3), 38.2 (CH_2), 40.9 (CHCO), 49.6 (NCH_2), 67.4 (CH), 99.1 (COSi), 122.8, 123.7, 129.9, 132.3, 132.9, 145.1 (aromatic), 169.8, 209.8 (C=O); MS *m/z* (relative intensity) 331 (m, 33), 316 (13), 234 (15), 233 (66), 232 (100), 186 (25); HRMS *m/z* 331.1604 ($C_{18}H_{25}NO_3Si$ requires 331.1605).

In MeCN Containing Dimethyl Maleate. A solution of **3** (400 mg, 1.71 mmol) and dimethyl maleate (284 mg, 1.97 mmol in 200 mL of acetone) was irradiated through a Pyrex filter under N_2 purging for 100 min (80% conversion of **3**), worked up, and purified in the manner described above. This gave 84 mg (16%) of **15**, 76 mg (15%) of **16**, and 300 mg (58%) of **17**.

15: ^{1}H-NMR −0.16 (s, 9 H, $Si(CH_3)_3$), 3.18 (s, 3 H, $SiOCCH(CO_2CH_3)$), 3.70 (d of d of d, 1 H, J = 11.7, 9.2 and 1.9 Hz, $CH(CO_2CH_3)$), 3.79 (s, 3 H, OCH_3)), 3.90 (d, 1 H, J = 1.9 Hz, $CCH(CO_2CH_3)$), 3.98 (d of d, 1 H, NCH_2), 4.22 (d of d, 1 H, J = 11.7 and 9.2 Hz, NCH_2), 7.47−7.56 (m, 3 H, aromatic), 7.69−7.71 (m, 1 H, aromatic); ^{13}C-NMR 0.7 ($Si(CH_3)_3$), 43.1 (CH_2), 49.3 (CH), 51.8 and 52.2 (CO_2CH_3), 57.0 (CH), 98.6 (quaternary C-3), 123.5, 123.8, 130.3, and 132.2 (aromatic, CH), 132.5 and 143.6 (aromatic, C), 169.1 (imide, C=O), 170.3 and 171.8 (ester, C=O); IR (KBr) 1720 cm^{-1} (strong C=O stretching); MS *m/z* (relative intensity) 377 (M^+, 7), 362 (M^+ − CH_3, 6), 287 (20), 255 (19), 232 (85), 228 (75); HRMS *m/z* 377.1283 ($C_{18}H_{23}NO_6Si$ requires 377.1295).

16: ^{1}H-NMR −0.19 (s, 9H, $Si(CH_3)_3$), 3.09 (d, 1 H, J = 10.7 Hz, $CCH(CO_2CH_3)$), 3.68 (s, 3 H, CO_2CH_3), 3.68−3.73 (m, 1 H, $CH(CO_2CH_3)$), 3.80−3.87 (m, 1 H, NCH_2), 3.82 (s, 3 H, OCH_3), 4.17−4.25 (m, 1 H, NCH_2), 7.48−7.74 (m, 4 H, aromatic); ^{13}C-NMR 0.5 ($Si(CH_3)_3$), 43.3 (CH_2), 47.7 (CH), 52.2 and 52.4 (CO_2CH_3), 55.3 (CH), 96.6 (quaternary, C-3), 123.6, 124.3, 130.2 and 132.9 (aromatic, CH), 130.4 and 146.2 (aromatic, C), 168.5 (imide, C=O), 169.6 and 172.3 (ester, C=O); IR (neat) 1741 (C=O stretching); MS *m/z* (relative intensity) 377 (M^+, 14), 362 (M^+ − CH_3), 318 (2), 308 (4), 256 (12), 232 (100), 228 (55), 204 (13), 169 (30); HRMS *m/z* 377.1288 ($C_{18}H_{23}NO_6Si$ requires 377.1295).

17: ^{1}H-NMR −0.15 ($Si(CH_3)_3$), 3.08 (s, 3 H, $CCH(CO_2CH_2)$), 3.59 (d, 1 H, J = 6.6 Hz, $CCH(CO_2CH_3)$), 3.67 (s, 3 H, OCH_3)), 3.69 (dd, 1 H, J = 10.3, 10.3 Hz, NCH_2), 4.07 (dd, 1 H, J = 6.6, 10.3 Hz, $CH(CO_2CH_3)$), 4.20 (dd, 1 H, J = 10.3, 10.3 Hz, NCH_2), 7.43−7.69 (m, 4 H, aromatic); ^{13}C-NMR 0.6 ($Si(CH_3)_3$), 43.8 (CH_2), 48.9 (CH), 52.27 and 52.31 (CO_2CH_3), 55.3 (CH), 98.7 (quaternary, C-3), 123.5, 123.7, 130.3, and 132.5 (aromatic, CH), 132.7 and 143.9 (aromatic, C), 169.6 (ester C=O), 170.1 (imide C=O), 171.3 (ester C=O); IR (KBr) 1730 and 1720 (C=O stretching); MS *m/z* (relative intensity) 377 (M^+, 13), 362 ($M^+ - CH_3$, 2), 346 (3), 302 (6), 288 (8), 232 (100), 228 (28); HRMS *m/z* (relative intensity) 377.1318 ($C_{18}H_{23}O_6NSi$ requires 377.1295).

In MeCN Containing Dimethyl Fumarate. A solution of **3** (400 mg, 1.71 mmol) and dimethyl maleate (284 mg, 1.97 mmol in 200 mL of acetone) was irradiated through a Pyrex filter under N_2 purging for 25 h (100% conversion of **3**), worked up, and purified in the manner described above. This gave 301 mg (47%) of **15** and 157 mg (24%) of **16**.

In Acetone Containing Methyl Acrylate. Six solutions, containing 40 mg each (0.17 mmol) of **3** in 20 mL of acetone and respectively 80, 40, 16, 8, 4, and 0.8 mM methyl acrylate and purged with N_2, were simultaneously irradiated for 3 h with Pyrex-filtered light. Workup and analysis of the product mixture gave the results summarized in the Discussion section above.

Preparation of 4-Methoxy-*N*-[(trimethylsilyl)methyl]phthalimide (18). 4-Methoxyphthalimide (**18**) was prepared from commercial dimethyl 4-methoxyphthalate (3 mL, 10.9 mmol) by the known method,[1] followed by N-silylmethylation with NaH and (trimethylsilyl)-methyl iodide. Chromatographic purification (silica gel, 1:1 ether−hexane) gave 0.43 g of the 4-methoxy-*N*-[(trimethylsilyl)methyl]-phthalimide (**18**) as an oil in a 15% overall yield: ^{1}H-NMR 0.06 (s, 9 H, $SiCH_3$), 3.12 (s, 2 H, CH_2), 3.87 (s, 3 H, OCH_3), 7.07 (dd, J = 8.2, 2.3 Hz, 1 H, aromatic), 7.25 (d, J = 2.3 Hz, 1 H, aromatic), 7.66 (d, J = 8.2 Hz, 1 H, aromatic); ^{13}C-NMR −1.9 ($SiCH_3$), 29.1 (CH_2), 55.9 (OCH_3), 107.9, 119.0, and 124.5 (aromatic, CH), 124.2, 134.9, and 170.3 (aromatic, ipso), 164.4 and 168.2 (NC=O); IR 2965, 2860, 1715, 1400, 1250, 850, 750; MS *m/z* (relative intensity) 263 (71), 262 (95), 249 (39), 248 (100), 234 (28), 233 (34), 232 (83), 160 (30), 73 (6); HRMS *m/z* 263.0968 ($C_{13}H_{17}NO_3Si$ requires 263.0987).

Irradiation of 18 and Acrylonitrile in MeCN. A solution of phthalimide **18** (60 mg, 0.23 mmol) and acrylonitrile (4.3 mL, 17.2 mmol) in 100 mL of CH_3CN was irradiated with Pyrex-filtered light under N_2 for 7.5 h (90% conversion of **18**), worked up, and purified as described above. This gave 7 mg (10%) of the adduct **19** as a single diastereomer and 3 mg (7%) of the known[1] desilylation product **21**.

A solution of 6 mg (0.02 mmol) of the phthalimide **18** and 0.03 mL (0.46 mmol) of acrylonitrile in 0.6 mL of CD_3CN in a sealed NMR tube was irradiated with Pyrex-filtered light for 31 h (80% conversion of **18**). The reaction progress was monitored by ^{1}H-NMR. The yields of photoproducts **19** and **21** were determined (1.3 mg of 4-nitro-*N*-[(trimethylsilyl)methyl]phthalimide as an internal standard) to be 21% and 17%, respectively, by integration of resonances at 7.1 ppm for **19**, 7.3 ppm for **21**, and 7.9−8.6 ppm for the internal standard.

19: ^{1}H-NMR −0.12 (s, 9 H, $SiCH_3$), 2.58 (m, 1 H, CH_2CH_2N), 2.86 (m, 1 H, CH_2CH_2N), 3.33 (d, J = 6.7 Hz, 1 H, CHCN), 3.46 (m, 1 H, CH_2N), 3.87 (m, 1 H, CH_2N), 3.89 (s, 3 H, OCH_3), 7.03 (s, 1 H, aromatic), 7.04 (d, J = 7.9 Hz, 1 H, aromatic), 7.68 (d, J = 7.9 Hz, 1 H, aromatic); ^{13}C-NMR 0.5 ($SiCH_3$), 32.3 (CH_2CH_2N), 39.8 (CHCN), 41.3 (CH_2N), 55.8 (OCH_3), 97.7 (COTMS), 117.3 (CN), 108.2, 116.8, and 125.6 (aromatic, CH), 124.5, 146.7, and 170.2 (aromatic, ipso), 164.1 (NCO); IR 2990, 2250, 1720, 1620, 1100, 870, 850; MS *m/z* (relative intensity) 316 (M, 34), 301 (22), 263 (28), 262 (35), 248 (12), 233 (19), 232 (100), 227 (25), 207 (11), 126 (13); HRMS *m/z* 316.1250 ($C_{16}H_{20}N_2O_3Si$ requires 316.1243).

Preparation of 4-Carbomethoxy(N-trimethylsilylmethyl)Phthalimide (22). 4-Carbomethoxy-*N*-[(trimethylsilyl)methyl]phthalimide was prepared from the known[1] 4-carbomethoxyphthalimide (4.0 g, 19.5 mmol) by silylmethylation with NaH and (iodomethyl)trimethylsilane. Chromatographic purification (silica gel, 1:1 ether−hexane) gave 3.1 g (10.7 mmol, 55%) of **22** (mp 43−45 °C, $CHCl_3$): ^{1}H-NMR 0.09 (s, 9 H, $SiCH_3$), 3.20 (s, 2 H, CH_2), 3.96 (s, 3 H, CO_2CH_3), 7.86 (d, J = 7.7 Hz, 1 H, aromatic), 8.36 (dd, J = 7.7, 1.3 Hz, 1 H, aromatic), 8.42 (d, J = 1.3 Hz, 1 H aromatic); ^{13}C-NMR −1.9 ($SiCH_3$), 29.5 (CH_2), 52.7 (OCH_3), 122.9, 123.9, and 135.1 (aromatic, CH), 132.5, 135.2, and 135.6 (aromatic, ipso), 165.2 and 167.4 (CO_2 and NC=O); IR 2970, 2910, 1730, 1410, 1390, 1300, 1250, 850, 730; MS *m/z* (relative intensity) 291 (M, 6), 290 (23), 276 (100), 232 (94), 188 (16), 103 (14), 73 (79); HRMS *m/z* 291.0889 ($C_{14}H_{17}NO_4Si$ requires 291.0927).

Irradiation of 22 and Acrylonitrile in MeCN. A solution of the 4-carbomethoxyphthalimide **22** (500 mg, 1.72 mmol) and acrylonitrile (4.3 mL, 17.2 mmol) in 200 mL of CH_3CN was irradiated with Pyrex-filtered light under N_2 for 25 h (44% conversion of **22**), worked up, and purified as described above. This gave 21 mg (21%) of a 1:1 inseparable mixture of cycloadducts **23** and **24** (24 mg, 30%), a 1:1 inseparable mixture of hydroxy adducts **25** and **26** (7 mg, 11%), the known[1] desilylation product **28**, 1 mg (1%) of the adduct **27**, and 139 mg of recovered **22**.

A solution of 15 mg (0.05 mmol) of the phthalimide **22** and 0.03 mL (0.46 mmol) of acrylonitrile in 0.6 mL of CD_3CN in a sealed NMR tube was irradiated with Pyrex-filtered light for 44 h (95% conversion). The reaction progress was monitored by ^{1}H-NMR. The yields of photoproducts **23**, **24**, **28**, and **27** were 33%, 34%, 20%, and 11%, respectively, by ^{1}H-NMR integration of resonances at 7.8 and 8.3 ppm for **23**, 7.8 and 8.2 ppm for **24**, 7.7 ppm for **28**, 7.8, 8.2, and 8.3 ppm for **27**, and 5.5 ppm for triphenylmethane (3 mg added as internal standard).

23: ^{1}H-NMR −0.14 (s, 9 H, $SiCH_3$), 2.67 (m, 1 H, CH_2CH_2N), 2.90 (m, 1 H, CH_2CH_2N), 3.40 (d, J = 5.7 Hz, 1 H, CHCN), 3.52 (m, 1 H, CH_2N), 3.87 (m, 1 H, CH_2N), 3.94 (s, 3 H, OCH_3), 7.68 (d, J = 7.9 Hz, 1 H, aromatic), 8.34 (d, J = 7.9 Hz, 1 H, aromatic), 8.43 (s, 1 H, aromatic); ^{13}C-NMR 0.5 ($SiCH_3$), 32.3 (CH_2CH_2N), 39.6 (CHCN), 41.1 (CH_2N), 52.6 (OCH_3), 97.9 (COTMS), 117.0 (CN), 123.2, 125.4, and 134.6 (aromatic, CH), 132.6, 133.1, and 148.2 (aromatic, *ipso*), 165.7 and 168.7 (NCO and CO_2CH_3); IR 2960, 2250, 1735, 1250−1350, 1100, 870, 850, 750.

24: ^{1}H-NMR −0.14 (s, 9H, $SiCH_3$), 2.67 (m, 1 H, CH_2CH_2N), 2.90 (m, 1 H, CH_2CH_2N), 3.40 (d, J = 5.7 Hz, 1 H, CHCN), 3.52 (m, 1 H, CH_2N), 3.87 (m, 1 H, CH_2N), 3.97 (s, 3 H, OCH_3), 7.83 (d, J = 7.6 Hz, 1 H, aromatic), 8.24 (s, 1 H, aromatic), 8.26 (d, J = 7.6 Hz, 1 H, aromatic); ^{13}C-NMR 0.5 ($SiCH_3$), 32.3 (CH_2CH_2N), 39.6 (CHCN), 41.2 (CH_2N), 52.7 (OCH_3), 97.9 (COTMS), 117.0 (CN), 124.1, 124.3, and 132.4 (aromatic, CH), 134.6, 135.9, and 144.3 (aromatic, ipso), 165.8 and 168.9 (NCO and CO_2CH_3); IR 2960, 2250, 1735, 1250−1350, 1100, 870, 850, 750.

25: ^{1}H-NMR 2.62 (m, 1 H CH_2CH_2N), 3.01 (m, 1 H, CH_2CH_2N), 3.46 (m, 2 H, CHCN and CH_2N), 3.84 (dt, J = 11.6, 8.5 Hz, 1 H, CH_2N), 3.91 (s, 3 H, OCH_3), 4.24 (s, 1 H, OH), 7.70 (d, J = 7.9 Hz, 1 H, aromatic), 8.24 (d, J = 1.5 Hz, 1 H, aromatic), 8.26 (dd, J = 7.9, 1.5 Hz, 1 H, aromatic); ^{13}C-NMR 32.6 (CH_2CH_2N), 37.5 (CHCN), 40.4 (CH_2N), 52.6 (OCH_3), 96.8 (COH), 117.1 (CN), 123.3, 125.1, and 134.8 (aromatic, CH), 132.3, 133.0, and 147.4 (aromatic, ipso), 165.6 and 168.3 (NCO and CO_2CH_3); IR 3400, 1730, 1685.

26: ^{1}H-NMR 2.62 (m, 1 H, CH_2CH_2N), 3.01 (m, 1 H, CH_2CH_2N), 3.46 (m, 2 H, CHCN and CH_2N), 3.84 (dt, J = 11.6, 8.5 Hz, 1 H, CH_2N), 3.92 (s, 3 H, OCH_3), 4.15 (s, 1 H, OH), 7.64 (d, J = 7.9 Hz, 1 H, aromatic), 8.10 (d, J = 1.3 Hz, 1 H, aromatic), 8.13 (dd, J = 7.9, 1.3 Hz, 1 H, aromatic); ^{13}C-NMR 32.6 (CH_2CH_2N), 37.4 (CHCN), 40.4 (CH_2N), 52.8 (OCH_3), 96.8 (COH), 117.0 (CN), 123.9, 124.3, and 132.4 (aromatic, CH), 134.6, 135.7, and 143.5 (aromatic, ipso), 165.6 and 168.5 (NCO and CO_2CH_3); IR 3400, 1730, 1685.

27: ^{1}H-NMR −0.08 (s, 9 H, $SiCH_3$), 2.50 (dd, J = 12.1, 7.4 Hz, 1 H, CHCN), 2.74 (m, 1 H, $CHCH_2$), 2.89 (m, 1 H, $CHCH_2$), 3.51 (m, 1 H, CH_2N), 3.78 (m, 1 H, CH_2N), 3.95 (s, 3 H, OCH_3), 7.81 (d, J = 7.9 Hz, 1 H, aromatic), 8.33 (dd, J = 7.9, 1.4 Hz, 1 H, aromatic), 8.39 (d, J = 1.4 Hz, 1 H, aromatic); ^{13}C-NMR 0.6 ($SiCH_3$), 32.0 (CH_2CH), 39.2 (CHCN), 41.1 (CH_2N), 52.6 (OCH_3), 95.3 (COTMS), 116.8 (CN), 123.0, 125.5, and 134.7 (aromatic, CH), 131.6, 133.1, and 148.9 (aromatic, ipso), 165.6 and 168.7 (NCO and CO_2CH_3); IR 2980, 2260, 1730, 1300, 850; MS *m/z* (relative intensity) 344 (M, 100), 329 (75), 291 (35), 276 (96), 267 (23), 255 (31), 232 (41), 223 (36), 207 (62), 126 (32); HRMS *m/z* 344.1205 ($C_{17}H_{20}N_2O_4Si$ requires 344.1192).

Elimination Reactions of 23 and 27 to Produce 29. A solution of a mixture of the adducts **23** and **24** (45 mg, 0.13 mmol) in 2 mL of THF containing concentrated H_2SO_4 (7.0 μL, 0.13 mmol) was stirred

at 80 °C for 2 h. Addition of K_2CO_3 and H_2O was followed by extraction with ether. The organic layer was dried and concentrated *in vacuo* to yield 33 mg of an inseparable mixture of two regioisomeric substances. Analysis of the spectroscopic data from this mixture gave the following properties for **29**. Also, the adduct **27** (25 mg, 0.07 mmol), when subjected to the above reaction and workup conditions, gave **29** (60%) exclusively.

29: ^{1}H-NMR 3.39 (t, J = 8.3 Hz, 2 H, CH_2CH$_2$N), 3.96 (s, 3 H, OCH$_3$), 4.03 (t, J = 8.3 Hz, 2 H, CH$_2$N), 7.86 (d, J = 8.0 Hz, 1 H, aromatic), 8.28 (d, J = 8.0 Hz, aromatic), 8.50 (s, 1 H, aromatic); ^{13}C-NMR 35.2 (*C*H$_2$CH$_2$N), 40.7 (CH$_2$N), 52.8 (OCH$_3$), 86.4 (*C*CN), 115.0 (CN), 123.2, 125.1, and 133.5 (CH, aromatic), 134.0 (*C*=CCN), 128.1 135.9, and 152.0 (aromatic, ipso), 161.8 and 165.3 (NCO and CO$_2$CH$_3$); MS *m/z* (relative intensity) 254 (M, 100), 253 (57), 223 (21), 195 (12), 167 (14), 140 (6); HRMS *m/z* 254.0686 ($C_{14}H_{10}N_2O_3$ requires 254.0691).

***N*-[(Trimethylsilyl)methyl]-1,8-naphthalimide (30).** A solution of 1,8-naphthalimide (1.5 g, 8.4 mmol) and NaH (0.22 g, 9.2 mmol) in 30 mL of DMF was stirred at 105 °C for 24 h. To this mixture at 110 °C was added (chloromethyl)trimethylsilane (1.03 g, 8.4 mmol), and stirring was continued for 7 h when the mixture was concentrated in vacuo. The residue was subjected to chromatography (silica, 1:4 EtOAc−hexane) to give 1.92 g (80%) of naphthalimide **30** (mp 130−131 °C): ^{1}H-NMR 0.09 (s, 9 H, SiMe$_3$), 3.74 (s, 2 H, CH$_2$N), 7.67−8.57 (m, 6 H, aromatic); ^{13}C-NMR −1.46 (SiMe$_3$), 31.8 (CH$_2$Si), 122.8, 126.8, 127.0, 131.0, 131.6, 133.6 (aromatic), 164.0 (C=O); IR 1690; MS *m/z* (relative intensity) 283 (m, 20), 282 (53), 268 (37), 219 (24), 181 (98), 169 (52), 131 (100), 119 (78); HRMS *m/z* 283.1028 ($C_{16}H_{17}NO_2Si$ requires 283.1029); UV (MeCN) 242 nm (4020), 335 nm (4040).

Photochemistry of *N*-[(Trimethylsilyl)methyl]-1,8-naphthalimide (30). Independent N_2-purged solutions containing 400 mg (1.41 mmol) of the naphthalimide **30** in 200 mL of either acetone, CH$_3$CN, or CH$_3$OH were irradiated for 12 h (66% of conversion of **30**), 17 h (79%), and 4.5 h (96%), respectively, by using Pyrex-filtered light. The residues obtained by concentration of the photolysates were chromatographed (silica, 1:4 EtOAc−hexane) to give 61 mg (39%), 132 mg (56%), and 215 mg (75%) of *N*-methylnaphthalimide **31**.

In MeCN Containing Methyl Acrylate or Acrylonitrile. Independent N_2-purged solutions of the naphthalimide **30** (400 mg, 1.41 mmol) in 200 mL of MeCN containing methyl acrylate (1.22 g, 14.1 mmol) and acrylonitrile (0.75 g, 14.1 mmol) were irradiated for 2.5 h by using Vycor-filtered light. Concentration of the photolysates gave residues, which were subjected to chromatography (silica, 1:1 EtOAc−hexane) to yield 130 mg (49%) of *N*-methylnaphthalimide **31** and 59 mg (17%) of the adduct **32**, and 131 mg (50%) of **31** and 53 mg (18%) of the adduct **33**, respectively.

32: ^{1}H-NMR 3.12 (t, J = 9.5 Hz, 2 H, CH$_2$C=), 3.83 (s, 3 H, OCH$_3$), 4.18 (t, J = 9.5 Hz, 2 H, NCH$_2$), 7.58−7.68 (m, 2 H, aromatic), 7.95−8.06 (m, 2 H, aromatic), 8.40 (dd, J = 7.2, 1.2 Hz, 1 H, aromatic), 9.81 (d, J = 7.2 Hz, 1 H, aromatic); ^{13}C-NMR 29.6 (NCH$_2$), 43.8 (CH$_2$C=), 51.7 (OCH$_3$), 110.9 (C=), 121.3, 124.0, 132.4, 134.3, 126.3, 126.6, 127.5, 131.0, 131.4, 133.0 (aromatic), 160.0 (C=O); IR 1710, 1675; UV (MeCN) 227 nm (15 100), 161 nm (12 100), 397 nm (8320); HRMS *m/z* 279.0908 (M, $C_{17}H_{13}NO_3$ requires 279.0895).

33: ^{1}H-NMR 3.09 (t, J = 9.4 Hz, 2 H, CH$_2$C=), 4.26 (t, J = 9.4 Hz, 2 H, NCH$_2$), 7.60−7.68 (m, 2 H, aromatic), 7.98−8.05 (m, 2 H, aromatic), 8.39 (dd, J = 7.2, 1.1 Hz, 1 H, aromatic), 8.78 (d, J = 7.2 Hz, 1 H, aromatic); ^{13}C-NMR 28.8 (CH$_2$C=), 44.4 (NCH$_2$), 85.4 (C≡N), 118.4 (C=), 120.1, 124.1, 128.6, 132.4, 126.5, 126.7, 127.0, 128.2, 131.8, 133.0 (aromatic), 148.9 (C=), 160.0 (C=O); IR 2170, 1670; UV (MeCN) 230 nm (10 100), 394 nm (9160); HRMS *m/z* 245.0717 (M − 1, $C_{16}H_9N_2O$ requires 245.0715).

Photochemistry of *N*-Phthaloylglycine (37). With Methyl Acrylate in CH$_3$CN. A solution of *N*-phthaloylglycine (**37**) (530 mg, 2.58 mmol) and methyl acrylate (2.32 mL, 25.8 mmol) in 200 mL of CH$_3$CN was irradiated through a Vycor filter under N_2 purging for 9 h (100% conversion of **37**), worked up, and purified in the manner described above. This gave 200 mg (48%) of *N*-methylphthalimide (**4**) along with the adducts **38** (220 mg, 34%, mp 110−112 °C) and **40** (30 mg, 5%, mp 182−186 °C).

38: ^{1}H-NMR 2.43 (m, 1 H, CH_2CH$_2$N), 2.72 (m, 1 H, CH_2CH$_2$N), 3.10 (s, 3 H, CO$_2$CH$_3$), 3.23 (dd, 1 H, J = 10.0, 10.0 Hz, CH$_2$CH_2N), 3.32 (d, 1 H, J = 7.0 Hz, CH(CO$_2$CH$_3$)), 3.74 (dd, 1 H, J = 9.3, 19.4 Hz, CH$_2$CH_2N), 4.31 (s, 1 H, OH), 7.33−7.57 (m, 4 H, aromatic); ^{13}C-NMR 31.0 (CH$_2$), 41.0 (CH$_2$N), 50.2 (CO$_2$*C*H$_3$), 51.4 (CH), 97.8 (COH), 123.0, 123.3, 129.9, 132.4, 132.4, 144.0 (aromatic), 170.1 (C=O), 171.6 (C=O); IR (KBr) 3200−3600 (OH stretching), 1735 (ester C=O stretching) and 1696 cm^{-1} (imide C=O stretching); MS *m/z* (relative intensity) 247 (M$^+$, 33), 230 (M$^+$ − OH, 9), 216 (10), 187 (81), 170 (12), 161 (100); HRMS *m/z* 247.0851 ($C_{13}H_{13}NO_4$ requires 247.0845).

40: ^{1}H-NMR 2.55−2.62 (m, 1 H, CH_2CH$_2$N), 2.75 (dd, 1 H, J = 11.8 and 8.1 Hz, C(OH)CH), 2.89−2.98 (m, 1 H, NCH_2CH$_2$), 3.49 (br s, 1 H, OH), 3.54−3.59 (m, 1 H, CH_2CH$_2$N), 3.71−3.78 (m, 1 H, NCH_2CH$_2$), 3.85 (s, 3 H, CO$_2$CH_3), 7.50−7.72 (m, 4 H, aromatic); ^{13}C-NMR 30.1 (*C*H$_2$CH$_2$N), 40.3 (CH$_2$N), 50.0 (CO$_2$*C*H$_3$), 52.4 (CH), 95.0 (C−OH), 123.5, 123.6, 130.2, and 132.9 (CH, aromatic), 131.6 and 145.8 (C, aromatic), 169.5 (imide C=O), 171.2 (*C*O$_2$CH$_3$); MS *m/z* (relative intensity), 247 (M$^+$, 10), 230 (M$^+$ − OH, 10), 229 (M$^+$ − H$_2$O, 40), 198 (M$^+$ − H$_2$O − OCH$_3$, 18), 188 (12), 187 (59), 171 (13), 170 (51), 161 (100), 160 (31), 142 (10); HRMS *m/z* 247.0852 ($C_{13}H_{13}NO_4$ requires 247.0845).

Independent treatment of adducts **38** and **40** with dilute aqueous HCl at 25 °C leads in each case to production of the dehydration product **42**: ^{1}H-NMR 3.34 (t, 2 H, J = 8.3 Hz, CH_2CH$_2$N), 3.90 (s, 3 H, CO$_2$CH$_3$), 3.95 (t, 2 H, J = 8.3 Hz, CH$_2$N), 7.59−7.66 (m, 2 H, aromatic), 7.82−7.87 (m, 1 H, aromatic), 8.51−8.56 (m, 1 H, aromatic); ^{13}C-NMR 34.4 (CH$_2$N), 40.4 (*C*H$_2$C=), 52.2 (OCH$_3$), 110.3 (C=), 112.8 (C=), 123.8, 127.1, 131.8, and 132.5 (CH, aromatic), 130.0 and 136.7 (C, aromatic), 162.1 (C=O); Ir (KBr) 1705 (conjugated C=O ester) and 1645; MS *m/z* (relative intensity) 230 (M$^+$ − 1, 8), 229 (M$^+$, 56), 214 (M$^+$ − CH$_3$, 12), 198 (M$^+$ − OCH$_3$, 29), 170 (M$^+$ − CO$_2$CH$_3$, 100), 143 (22), 142 (36), 115 (85); HRMS *m/z* 229.0729 ($C_{13}H_{11}NO_3$ requires 229.0739).

With Acrylonitrile in CH$_3$CN. A solution of *N*-phthaloylglycine (**37**) (500 mg, 2.44 mmol) and acrylonitrile (1.61 mL, 24.4 mmol) in 200 mL of CH$_3$CN was irradiated through a Vycor filter under N_2 purging for 9 h (100% conversion of **37**), worked up, and purified in the manner described above. This gave 70 mg (18%) of *N*-methylphthalimide (**4**) and adducts **39** (270 mg, 51%, mp 202−203 °C) and **41** (120 mg, 23%, mp 189−193 °C).

39: ^{1}H-NMR (CD$_3$CN) 2.59 (m, 1 H, CH_2CH$_2$N), 2.92 (m, 1 H, CH_2CH$_2$N), 3.47 (dd, 1 H, J = 10.0, 10.0 Hz, CH$_2$CH_2N), 3.54 (d, 1 H, J = 6.5 Hz, CHCN), 3.76 (dd, 1 H, J = 10.0, 18.9 Hz, CH$_2$CH_2N), 4.76 (s, 1 H, OH, 7.55−7.72 (m, 4 H, aromatic); ^{13}C-NMR (CD$_3$CN) 33.4 (CH$_2$), 38.8 (*C*HCN), 41.0 (CH$_2$N), 97.9 (C(OH)), 119.3 (CN), 124.0, 124.3, 131.7, and 134.2 (CH, aromatic), 133.4 and 145.4 (C, aromatic), 170.2 (C=O); IR (KBr) 3200−3400 (OH stretching), 2241 (C≡N stretching), 1671 (imide C=O stretching); MS *m/z* (relative intensity) 214 (M$^+$, 29), 197 (M$^+$ − OH, 10), 186 (29), 161 (100), 148 (13), 132 (34); HRMS *m/z* 214.0745 ($C_{12}H_{10}N_2O_2$ requires 214.0742).

41; ^{1}H-NMR 2.62 (dd, 1 H, J = 12.0 and 7.8 Hz, CHCN), 2.76−2.79 (m, 1 H, CH_2CH$_2$N), 2.88 (br s, 1 H, OH), 2.94−3.03 (m, 1 H, CH$_2$CH_2N), 3.58−3.61 (m, 1 H, CH_2CH$_2$N), 3.71−3.76 (m, 1 H, CH$_2$CH_2N), 7.56−7.80 (m, 4 H, aromatic); ^{13}C-NMR 32.4 (*C*H$_2$CH$_2$N), 37.3 (*C*HCN), 40.8 (CH$_2$N), 94.6 (CH(OH)), 117.2 (CN), 122.9, 124.4, 131.4, 133.9 (CH, aromatic), 144.2 (C, aromatic), 169.6 (C=O); MS *m/z* (relative intensity), 214 (M$^+$, 21), 197 (M$^+$ − OH, 14), 196 (M$^+$ − H$_2$O, 89), 186 (22), 170 (17), 168 (21), 167 (45), 161 (48), 160 (100), 149 (71); HRMS *m/z* 214.0740 ($C_{12}H_{10}N_2O_2$ requires 214.0742).

Photochemistry of *N*-Phthaloylalanine (44) with Methyl Acrylate in MeCN. A solution of *N*-phthaloylalanine (**44**, 1.0 g, 4.6 mmol) and methyl acrylate (4.0 g, 45.6 mmol) in 200 mL of MeCN was irradiated with Vycor-filtered light under N_2 for 8 h (70% conversion of **44**). After removal of solvent and purification by column chromatography (silica gel, 1:3 EtOAc−hexane) were obtained 70 mg (9%) of **48**, 50 mg (9%) of **49**, 150 mg (18%) of **45**, 350 mg (42%) of **46**, and a trace amount of **47**.

45: mp 132−134 °C (acetone−hexane); ^{1}H-NMR 1.47 (d, 3 H, J = 6.4 Hz, CHCH_3), 2.61 (dd, 1 H, J = 8.2 and 7.8 Hz, CH(CO$_2$CH$_3$)), 2.71−2.77 (m, 2 H, CHCH_2CH), 3.63 (s, 1 H, OH), 3.82 (s, 3 H, CO$_2$CH$_3$), 4.01−4.04 (m, 1 H, CHCH$_3$), 7.44−7.69 (m, 4 H, aromatic); ^{13}C-NMR 22.9 (CHCH$_3$), 38.5 (CHCH$_2$CH), 50.1 (CO$_2$*C*H$_3$), 50.6 (*C*H(CO$_2$CH$_3$)), 52.3 (*C*HCH$_3$), 95.1 (C(OH)), 123.4, 123.7, 130.1, and

132.8 (CH, aromatic), 131.7 and 145.8 (aromatic, ipso), 169.8 (amide, C=O), 171.1 (ester, C=O); MS (CI) *m/z* (relative intensity) 262 ($M + H^+$, 23), 261 (M^+, 15), 230 ($M^+ - OCH_3$, 11), 228 (19), 212 ($M^+ - H_2O - OCH_3$, 14), 201 (15), 196 (20), 186 (14), 184 (32), 176 (14), 175 (100), 174 (31), 170 (16), 160 (34); HRMS (CI) *m/z* 262.1062 ($C_{14}H_{15}NO_4 + H^+$ requires 262.1079).

46: ^{1}H-NMR 1.48 (d, 3 H, J = 6.4 Hz, $CHCH_3$), 2.45 and 2.73 (dd, 1 H, J = 12.9 and 7.6 Hz, $CHCH_2CH$), 3.19 (s, 3 H, CO_2CH_3), 3.44 (d, J = 7.0 Hz, 1 H, $CH(CO_2CH_3)$), 3.67 (br s, 1 H, OH), 4.33 (sext, 1 H, J = 7.2 Hz, $CHCH_3$), 7.30−7.70 (m, 4 H, aromatic); MS *m/z* (relative intensity) 261 (M^+, 31), 243 (19), 175 (100), 130 (22), 77 (25); HRMS *m/z* 261.0991 ($C_{14}H_{15}NO_4$ requires 261.1001).

47: ^{1}H-NMR 1.52 (d, 3 H, J = 6.5 Hz, $CHCH_3$), 2.65 (dd, 1 H, J = 14.5 and 8.4 Hz, $CHCH_2CH$), 2.76 (d, 1 H, J = 7.1 Hz, $CH(CO_2CH_3)$), 2.76 (dd, 1 H, J = 14.5 and 7.1 Hz, $CHCH_2CH$), 3.50 (s, 1 H, OH), 3.86 (s, 3 H, CO_2CH_3), 4.01−4.13 (m, 1 H, $CHCH_3$), 7.50−7.75 (m, 4 H, aromatic); ^{13}C-NMR 23.5 ($CHCH_3$), 39.0 ($CHCH_2CH$), 50.7 (CO_2CH_3), 51.0 ($CH(CO_2CH_3)$), 53.9 ($CHCH_3$), 103.0 (C(OH)), 123.9, 124.2, 130.7, and 133.3 (CH, aromatic); IR (KBr) 1736 (ester C=O stretching), 1668 (amide C=O stretching); MS *m/z* (relative intensity) 261 (M^+, 7), 244 (M^+ − OH, 9), 243 ($M^+ - H_2O$, 30), 228 ($M^+ - H_2O - CH_3$, 17), 201 (14), 184 (33), 175 (100), 169 (15), 160 (15); HRMS *m/z* 261.0983 ($C_{14}H_{15}NO_4$ requires 261.1001).

48: ^{1}H-NMR 1.54 (d, 3 H, J = 6.4 Hz, $CHCH_3$), 2.89 (dd, 1 H, J = 17.2 and 4.7 Hz, $=CCH_2CH$), 3.55 (dd, 1 H, J = 17.2 and 9.6 Hz, $=CCH_2CH$), 3.88 (s, 3 H, CO_2CH_3), 4.47−4.51 (m, 1 H, $CHCH_3$), 7.57−7.64 (m, 2 H, aromatic), 7.81 (d, 1 H, J = 7.2 Hz, aromatic), 8.51 (d, 1 H, J = 7.5 Hz, aromatic); ^{13}C-NMR 20.3 ($CHCH_3$), 42.7 ($=CCH_2CH$), 49.6 (CO_2CH_3), 51.7 ($CHCH_3$), 108.5 ($=C(CO_2CH_3)$), 123.2, 126.5, 131.3, and 132.0 (CH, aromatic), 136.3 ($NC=C(CO_2CH_3)$), 129.3 and 148.4 (aromatic, ipso), 163.8 (amide, C=O), 165.1 (ester, C=O); IR (KBr) 1699 (ester C=O stretching), 1645 (amide C=O stretching); MS *m/z* (relative intensity) 243 (M^+, 27), 228 ($M^+ - CH_3$, 10), 184 ($M^+ - CO_2CH_3$, 12), 107 (12), 87 (11), 85 ($M^+ - CH_2 - CO_2CH_3$, 69), 83 ($C{=}CCO_2CH_3^+$, 100), 66 (15); HRMS *m/z* 243.0900 ($C_{14}H_{13}NO_3$ requires 243.0895).

Photochemistry of *N*-Phthaloylphenylalanine (50) with Methyl Acrylate in MeCN. A solution of *N*-phthaloyl-L-phenylalanine (**50**, 600 mg, 2.0 mmol) and methyl acrylate (1.7 g, 20.3 mmol) in 200 mL of MeCN was irradiated with Vycor-filtered light under N_2 for 6 h (70% conversion of **50**). After removal of solvent and purification by column chromatography (silica gel, 1:3 EtOAc−hexane) were obtained 50 mg (14%) of **54**, 30 mg (7%) of **53**, 80 mg (17%) of **52**, and 180 mg (38%) of **51**.

51: ^{1}H-NMR 2.45 (s, 1 H, OH), 2.50−2.69 (m, 2 H, $CHCH_2CH$), 3.00 and 3.32 (dd, 1 H, J = 13.2 and 8.8 Hz, CH_2Ph), 3.16 (s, 3 H, CO_2CH_3), 3.24 (d, 1 H, J = 4.5 Hz, $CH(CO_2CH_3)$), 4.45−4.62 (m, 1 H, $CHCH_2Ph$), 7.24−7.33 (m, 5 H, phenyl), 7.44−7.73 (m, 4 H, aromatic); ^{13}C-NMR 37.0 ($CHCH_2CH$), 42.9 ($PhCH_2$), 51.7 (CO_2CH_3), 52.0 ($CH(CO_2CH_3)$), 56.9 (CHBn), 98.2 (C(OH)), 123.7, 124.0, 124.2, 127.1, 130.0, 130.3, and 133.0 (CH, aromatic), 130.8, 138.3, and 144.3 (aromatic, ipso); MS *m/z* (relative intensity) 337 (M^+, 0.8), 320 (M^+ − OH, 3), 319 ($M^+ - H_2O$, 7), 288 (7), 246 (M^+ − Bn, 33), 228 ($M^+ - H_2O$ − Bn, 100), 227 (12), 214 (24), 196 (20), 186 (13), 184 (21); HRMS *m/z* 337.1299 ($C_{20}H_{19}NO_4$ requires 337.1314).

52: mp 192−194 °C (CH_2Cl_2−hexane); ^{1}H-NMR 2.50−2.70 (m, 2 H, $CHCH_2CH$), 2.75 (d, 1 H, J = 6.3 Hz, $CH(CO_2CH_3)$), 2.99 (dd, 1 H, J = 13.2 and 9.0 Hz, CH_2Ph), 3.28 (s, 1 H, OH), 3.35 (dd, 1 H, J = 13.2 and 4.8 Hz, CH_2Ph), 3.83 (s, 3 H, CO_2CH_3), 4.21−4.28 (m, 1 H, $CHCH_2Ph$), 7.26−7.46 (m, 5 H, phenyl), 7.47−7.74 (m, 4 H, aromatic); ^{13}C-NMR 36.4 ($CHCH_2CH$), 43.2 ($PhCH_2$), 50.9 (CO_2CH_3), 52.8 ($CH(CO_2CH_3)$), 55.9 (CHBn), 95.4 (C(OH)), 124.0, 124.2, 127.1, 129.0, 130.1, and 133.4 (CH, aromatic), 130.6, 138.2, and 146.3 (aromatic, ipso), 169.5 and 171.4 (NCO and CO); IR (KBr) 1747 (ester C=O stretching), 1685 (amide C=O stretching); MS *m/z* (relative intensity) 337 (M^+, 0.7), 320 (M^+ − OH, 3), 319 ($M^+ - H_2O$, 11), 288 (7), 246 (M^+ − Bn, 27), 228 ($M^+ - H_2O$ − Bn, 100), 214 (27), 196 (20), 186 (17), 184 (23), 168 (22); HRMS *m/z* 337.1314 ($C_{20}H_{19}NO_4$ requires 337.1314).

53: ^{1}H-NMR 2.93 (dd, 1 H, J = 13.6 and 9.3 Hz, CH_2Ph), 3.08 (dd, 1 H, J = 17.7 and 5.1 Hz, $=CCH_2$), 3.30 (dd, 1 H, J = 17.7 and 9.3 Hz, $=CCH_2$), 3.61 (dd, 1 H, J = 13.6 and 4.0 Hz, CH_2Ph), 4.57−4.64 (m, 1 H, $CHCH_2Ph$), 7.20−7.51 (m, 5 H, phenyl), 7.60−7.89 (m, 3 H, aromatic), 8.47−8.52 (m, 1 H, aromatic); ^{13}C-NMR 39.0 ($=CCH_2$), 39.5 ($PhCH_2$), 51.8 (CO_2CH_3), 54.7 (CHBn), 108.9 ($=C(CO_2CH_3)$), 123.5, 126.7, 126.9, 128.7, 128.8, and 132.3 (CH, aromatic), 128.8, 131.4, and 136.6 (aromatic, ipso), 134.6 ($NC=$), 164.0 (imide, C=O), 165.1 (ester, C=O); IR (KBr) 1733 and 1703 (C=O stretching); MS *m/z* (relative intensity) 319 (M^+, 9), 288 ($M^+ - OCH_3$, 7), 228 (M^+ − Bn, 100), 196 (11), 184 (21), 169 (29); HRMS *m/z* 319.1231 ($C_{20}H_{17}NO_3$ requires 319.1209).

Preparation of 2-Phthalimido-1-phenylethanol (55) and OTMS Derivative 56. A mixture of 2-bromoacetophenone (10 g, 50 mmol) and sodium borohydride (2.8 g, 75 mmol) in ethanol (10 mL) was stirred for 5 h at 0 °C and extracted with $CHCl_3$. After concentration of the organic layer *in vacuo* and column chromatography (hexane−$CHCl_3$, 5:1) of the residue, 9.7 g (96%) of 2-hydroxyphenethyl bromide was obtained: ^{1}H-NMR 2.88 (br s, 1 H, OH), 3.53 (d, 1 H, J = 7.7 Hz, diastereotopic CH_2Br), 3.56 (d, 1 H, J = 4.5 Hz, diastereotopic CH_2Br), 4.87 (dd, 1 H, J = 7.7 and 4.5 Hz, CH_2CH), 7.33 (br s, 5 H, aromatic); ^{13}C-NMR 40.0 (CH_2Br), 73.7 (CH), 125.9, 128.4 and 128.6 (CH, aromatic), 140.4 (C, aromatic); IR (neat) 3600−3200 (OH); MS *m/z* (relative intensity) 185 (M^+ − OH, 46.6), 183 (M^+ − OH, 47.5), 121 (M^+ − Br, 16), 107 ($M^+ - CH_2Br$, 100), 104 (31), 91 (28), 79 (90), 77 (74); HRMS *m/z* 184.9804 ($C_8H_9{}^{81}BrO$−OH requires 184.9789).

To a solution of chlorosilanetrimethyl (3.78 g, 35 mmol) in hexane (30 mL) was added a mixture of hexamethyldisilazane (4.67 g, 29 mmol) and 2-bromo-1-phenylethanol (5.87 g, 29 mmol) in hexane (30 mL). The resulting mixture was stirred at reflux for 10 h and filtered, and the precipitate was washed with hexane. After concentration of the filtrate *in vacuo* and column chromatography ($CHCl_3$) of the residue, 7.7 g (97%) of 2-[(trimethylsilyl)oxy]phenethyl bromide was obtained: ^{1}H-NMR 0.05 (s, 9 H, $SiMe_3$), 3.45 (d, 1 H, J = 7.4 Hz, diastereotopic CH_2Br), 3.45 (d, 1 H, J = 5.0 Hz, diastereotopic CH_2Br), 4.84 (dd, 1 H, J = 5.0 and 7.4 Hz, CH), 7.32−7.34 (s, 5 H, aromatic); ^{13}C-NMR 0.1 ($SiMe_3$), 39.3 (CH_2Br), 75.1 (CH), 126.1, 128.0, and 128.4 (CH, aromatic), 142.0 (C, aromatic); MS *m/z* (relative intensity) 259 ($M^+ - CH_3$, 11), 257 ($M^+ - CH_3$, 11), 193 (M^+ − Br, 13), 179 ($M^+ - CH_2Br$, 100), 139 (21), 137 (22), 104 (14), 73 (51); HRMS *m/z* 258.9974 ($C_{11}H_{17}{}^{81}BrSiO$−CH_3 requires 258.9977).

A solution of 2-[(trimethylsilyl)oxy]phenethyl bromide (7.4 g, 27 mmol) and potassium phthalimide (5.2 g, 28 mmol) in DMF (60 mL) was stirred at 80 °C for 4 h. Concentration *in vacuo* gave a residue, which was extracted with ethyl acetate. The organic layer was dried and concentrated *in vacuo* to give a solid, which was crystallized (mp 105−106 °C, ethanol) to yield 5.2 g (56%) of *N*-[2-[(trimethylsilyl)-oxy]phenethyl]phthalimide (**56**): ^{1}H-NMR 0.00 (s, 9 H, $SiMe_3$), 3.84 (dd, 1 H, J = 13.6 and 4.4 Hz, diastereotopic CH_2), 4.06 (dd, 1 H, J = 13.6 and 9.0 Hz, diastereotopic CH_2), 5.18 (dd, 1 H, J = 9.0 and 4.4 Hz, CH), 7.36−7.55 (m, 5 H, aromatic), 7.81−7.97 (m, 4 H, aromatic); ^{13}C-NMR −0.3 ($SiMe_3$), 46.2 (CH_2), 71.8 (CH), 123.2, 126.1, 127.7, 128.3, and 133.9 (CH, aromatic), 132.0 and 141.6 (C, aromatic), 168.1 (C=O); MS *m/z* (relative intensity), 339 (M^+, 0.1) 324 ($M^+ - CH_3$, 2), 233 (4), 204 (3), 180 (9), 179 ($PhCHOSi(CH_3)_3^+$, 71), 160 (8), 149 (3), 73 (100); HRMS *m/z* 339.1293 ($C_{19}H_{21}NO_3Si$ requires 339.1291).

Recrystallization (95% ethanol) of the OTMS derivative **56** obtained from a reaction under conditions identical to those described above gave 8.8 g (81%, mp 160−161 °C) of *N*-(2-hydroxyphenethyl)-phthalimide (**55**): ^{1}H-NMR 2.89 (br s, 1 H, OH), 3.92 (dd, 1 H, J = 14.3 and 3.6 Hz, diastereotopic CH_2), 4.00 (dd, 1 H, J = 14.3 and 8.6 Hz, diastereotopic, CH_2), 5.05 (dd, 1 H, J = 8.6 and 3.6 Hz, CH), 7.25−7.47 (m, 5 H, aromatic), 7.66−7.88 (m, 4 H, aromatic); ^{13}C-NMR 45.7 (CH_2), 72.6 (CH), 123.4, 125.9, 128.1, 128.6, and 134.1 (CH, aromatic), 131.8 and 141.0 (C, aromatic), 168.7 (C=O); IR (KBr) 3600−3200 (OH), 1702 (C=O); MS *m/z* (relative intensity), 267 (M^+, 13), 250 (M^+ − OH, 25), 163 (6), 162 (62), 161 (100), 132 (37), 120 (20), 117 (39), 107 ($PhCHOH^+$, 63), 105 (64), 104 (43); HRMS *m/z* 267.0888 ($C_{16}H_{13}NO_3$ requires 267.0896).

Photochemistry of 2-Phthalimido-1-phenylethanol (55). Irradiation in CH_3CN and Acetone. Solutions of *N*-(2-hydroxyphenethyl)-phthalimide (**55**) (300 mg, 1.12 mmol) in 100 mL of CH_3CN or 100 mL of acetone were independently irradiated using Pyrex-filtered light under N_2 purging. Removal of solvent and column chromatography

of the resulting residue gave the known *N*-methylphthalimide (**4**), phthalimidoacetophenone (**57**), and benzaldehyde. Reaction times, percent conversions of **55**, and product yields in CH_3CN and acetone are as follows: (CH_3CN) 10 h, 90%, **4** (37%) and **57** (3%); (acetone) 4 h, 95%, **4** (37%) and **57** (5%). Benzaldehyde was observed to be produced as a major product, and quantitative analysis of the resulting residue before column chromatography by ^{1}H-NMR showed that the yields of benzaldehyde are ca. 60%.

Irradiation of 55 in Acetone with Methyl Acrylate. A solution of **55** (530 mg, 2.0 mmol) and methyl acrylate (1.72 g, 20 mmol) in 100 mL of acetone was irradiated through a Pyrex filter under N_2 purging for 36 h (ca. 95% conversion of **55**). After removal of solvent, the residue was subjected to column chromatography (ethyl acetate−hexane, 1:4) to give adducts **38** (104 mg, 26%) and **40** (26 mg, 7%), *N*-methylphthalimide (**4**, 22 mg, 7%), and phthalimidoacetophenone (**57**, 20 mg, 4%).

Irradiation of 55 in Acetone with Acrylonitrile. A solution of **55** (300 mg, 1.12 mmol) and acrylonitrile (0.53 g, 10 mmol) in acetone (100 mL) was irradiated through a Pyrex filter under N_2 purging for 40 h (ca. 60% conversion of **55**). After removal of solvent, the residue was subjected to column chromatography (ethyl acetate−hexane, 1:4) to give *N*-methylphthalimide (**4**, 5 mg, 5%), phthalimidoacetophenone (**57**, 11 mg, 6%), and adducts **41** (12 mg, 9%) and **39** (9 mg, 6%).

Acetophenone Sensitization of the Photoreaction of *N*-[(Trimethylsilyl)methyl]phthalimide (3) with Methyl Acrylate in Acetonitrile. Two solutions, one of *N*-[(trimethylsilyl)methyl]phthalimide (**3**, 30 mg, 0,13 mmol), methyl acrylate (60 mg, 0.70 mmol), and acetophenone (70 mg, 0.58 mmol) in 15 mL of CH_3CN, and the other identical but without acetophenone, were irradiated simultaneously in Pyrex tubes with uranium glass-filtered light under N_2 for 7 h. The reaction mixtures were examined by TLC (ethyl acetate−hexane, 1:3), which showed that *N*-[(trimethylsilyl)methyl]phthalimide (**3**) from the photoreaction mixture containing acetophenone was almost completely consumed to produce exclusively adducts **10** and **11**. In contrast, the photoreaction mixture from irradiation of the solution not containing acetophenone contained only phthalimide **3** and none of the adducts **10** and **11**.

Quantum Yields for Photoreactions of *N*-[(Trimethylsilyl)methyl]-phthalimide (3) and *N*-Phthaloylglycine (37) with Methyl Acrylate. Quantum yields were measured by using a Rayonet photoreactor with 3000 Å light, and a 0.10 M benzophenone−benzhydrol mixture was employed as actinometer. Sealed solutions containing *N*-[(trimethylsilyl)methyl]phthalimide (**3**, 30 mg, 0.13 mmol) with two different concentrations of methyl acrylate (110 mg, 1.27 mmol and 55 mg, 0.63 mmol) and *N*-phthaloylglycine (**37**, 30 mg, 0.15 mmol) with methyl acrylate (110 mg, 1.27 mmol) were simultaneously irradiated for 70 min in a merry-go-round apparatus for 30 min (ca. 10−20% conversions). The crude photolysates obtained after concentration *in vacuo* were analyzed by ^{1}H-NMR to determine the yields for adduct formation. These data gave the following quantum yield for adduct formation: **10** + **11** from **3**, 4.2×10^{-3} (at 86 mM methyl acrylate) and 5.4×10^{-3} (at 43 mM methyl acrylate); **38** + **40** from **37**, 3.9×10^{-3} (at 86 mM methyl acrylate).

X-ray Crystal Structure Determinations for 12, 14, 45, and 52. All samples were mounted on thin Pyrex glass rods with a small quantity of quick-drying epoxy cement. Intensity data were collected on an Enraf-Nonius CAD4 diffractometer with the $\theta-2\theta$ scan technique. A HOG monochromator was used in the incident beam. The Mo and Cu wavelengths used were 0.710 69 Å and 1.541 78 Å, respectively. The structure solutions were performed on VaxStation II and 3100 workstations with the TEXSAN program system. Structure solutions were obtained with the MITHRIL subprogram of TEXSAN. Structure refinement was by full-matrix least squares. Hydrogen atoms were refined for **12**, **45**, and **52**. The calculations included a correction for secondard extinction. Crystallographic data for the four compounds are provided as supplementary material.

Acknowledgment. Support for this investigation from the NSF (CHE-17725, INT-17290 for P.S.M.) and KOSEF (International Cooperative Research and CBM of POSTECH for U.C.Y.) is acknowledged.

Supplementary Material Available: X-ray crystallographic data for compounds **12**, **14**, **45**, and **52** (Tables 1− 16) (27 pages); structure factors (75 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

JA943512K