Mechanistic Studies of the Azomethine Ylide-Forming Photoreactions of *N*-(Silylmethyl)phthalimides and *N*-Phthaloylglycine

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Abstract: In earlier studies we have shown that irradiation of MeCN solutions of *N*-[(trimethylsilyl)methyl]-phthalimide and *N*-phthaloylglycine in the presence of electron-defecient olefins (e.g., methyl acrylate) results in the production of cycloadducts. In addition, irradiation of these substances in aqueous MeCN leads to formation of *N*-methylphthalimide. Laser flash photolysis and fluorescence spectroscopy have now been employed to investigate the mechanistic details of these novel excited-state processes. The results of this effort show that azomethine ylides are the key reactive intermediates in these processes. In addition, the investigations provide information about the dynamics of several ylide decay pathways and the nature of the excited states responsible for the ylide-forming silyl-migration (singlet and triplet) and decarboxylation (triplet) reactions. Pulsed irradiations of MeCN solutions of *N*-[(trimethylsilyl)methyl]phthalimide (**1**) and *N*-phthaloylglycine (**2**) give rise to transients whose absorption and decay properties are consistent with their assignment as azomethine ylides. Kinetic analysis of the decay of the ylides in the presence of dipolarophiles, methyl acrylate and acrylonitrile, provides the rates of the dipolar cycloaddition reactions. Reactions of methyl acrylate with the ylides produced by pulsed irradiation of *N*-[(trimethylsilyl)methyl]phthalimide (**1**) and *N*-phthaloylglycine (**2**) occur with respective bimolecular rate constants of 8.9×10^6 and 2.7×10^7 M^{-1} s^{-1}. Methanol promotes the decay of the *N*-[(trimethylsilyl)methyl]phthalimide-derived ylide by a process which is second order in MeOH and has a kinetic OD-isotope effect of 4.3. In contrast, quenching of this ylide by acetic acid is first order in AcOH. The results suggest that the mechanism for MeOH-promoted decay involves initial and reversible formation of a silylate complex via nucleophilic addition of MeOH to the ylide. This is then followed by rate-limiting proton transfer from MeOH to the carbanionic center in the silylate complex either in concert with or preceding desilylation. The mechanism for AcOH-induced ylide decay has these steps reversed; i.e., rate-limiting proton transfer precedes AcOH-induced desilylation. Also, MeOH catalyzes the decay of the ylide derived by irradiation of *N*-phthaloylglycine by a process which is first order in MeOH and has a kinetic OD-isotope effect of 1.5. Finally, the observations (1) of complete loss of fluorescence of the 1,8- and 2,3-naphthalimide chromophores upon changing the N-substituent from methyl to (trimethylsilyl)methyl and (2) that ylide formation from **1** can be xanthone triplet sensitized suggest that the ylide-forming, silyl-transfer reactions of the (silylmethyl)phthalimides can occur in both the singlet and triplet excited-state manifolds.

Introduction

In recent publications,[1] we described a novel class of photocycloaddition reactions of *N*-(silylmethyl)phthalimides and -maleimides that result in the production of functionalized pyrrolizidines. An example is found in the photoreaction of *N*-[(trimethylsilyl)methyl]phthalimide (**1**)[1b] with methyl acrylate, which produces the benzopyrrolizidine **5** exclusively. We have suggested that it is likely that these processes follow a mechanistic route involving generation and endo-selective trapping of azomethine ylides related to **3** (Scheme 1). Additional evidence supporting the proposal that ylides are short-lived intermediates in these pathways comes from the observation that irradiation of **1** in a D_2O−MeCN solution leads to formation of the *N*-(monodeuteriomethyl)phthalimide (**7**).[1b] This product is expected to form by ylide protonation−desilylation (or the reverse).

A major process involved in the photochemistry of *N*-phthaloyl α-amino acids involves decarboxylation to produce the corresponding *N*-alkylphthalimide[2] (e.g., the transformation of **2** to **8**, Scheme 1). Observations made in our earlier and more recent[2d] studies suggest that these photoreactions also proceed via the intermediacy of azomethine ylides (e.g., **4**). Collapse of **4** by a 1,4-hydrogen shift pathway would give rise to the *N*-alkyl products. Consistent with this proposal is our finding that

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(1) (a) Yoon, U. C..; Kim, D. U.; Kim, J. C.; Lee, C. W.; Choi, Y. S.; Mariano, P. S.; Lee, Y. J.; Ammon, H. L. *Tetrahedron. Lett.* **1993**, *34*, 5859. (b) Yoon, U. C.; Kim, D. U..; Lee, J. G.; Lee, Y. J.; Ammon, H. L.; Mariano, P. S. *J. Am. Chem. Soc.* **1995**, *117*, 2698. (c) Yoon, U. C.; Choi, S. J.; Lee, Y. J.; Mancheno, M. J.; Mariano, P. S. *J. Org. Chem.* **1995**, *60*, 2353. (d) Yoon, U. C.; Lee, C. W.; Oh, S. W.; Mariano, P. S. Unpublished results.

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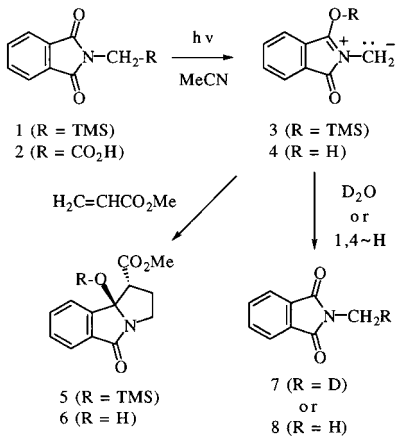
Scheme 1



irradiation of these amino acid derivatives in solutions containing dipolarophiles (e.g., methyl acrylate) leads to formation of benzopyrrolizidine cycloadducts (e.g., **6**, Scheme 1).[1b,d]

Our continuing studies of these novel and preparatively significant photochemical processes have focused on both mechanistic and synthetic issues. In this paper, we report the results of photophysical investigations which (1) evidence the existence of ylide intermediates in the silyl-transfer and decarboxylation photoreactions, (2) provide data on the dynamics of various ylide decay pathways, and (3) suggest the nature of the phthalimide excited states which are responsible for the silyl-transfer reaction.

Results

Laser flash photolysis (LFP) experiments were carried out with *N*-[(trimethylsilyl)methyl]phthalimide (**1**) and *N*-phthaloylglycine (**2**). Pulsed 266 or 308 nm irradiation of N_2-saturated MeCN solutions of **1** (5 mM) at 25 °C results in the formation of a transient with an absorption maximum at 392 nm (Figure 1). The UV-absorption and kinetic data (see below) are consistent with the assignment of the 392 nm transient as the azomethine ylide **3**. Decay of this transient in MeCN follows second-order kinetics (1.4×10^6 A^{-1} s^{-1}) (Figure 2). Analyses of the effects of acrylonitrile (Figure 1, inset) and methyl acrylate on the decay rates give the second-order rate constants for trapping of ylide **3** by these dipolarophiles (1.2×10^7 and 8.9×10^6 M^{-1} s^{-1}, respectively) (Table 1). Methanol (and MeOD) also promote decay of the 392 nm transient. The observed rate vs MeOH concentration data best fit a process that is second order in this alcohol (Figure 3). The rate constants for MeOH (1.9×10^5 M^{-2} s^{-1}) and MeOD (4.4×10^4 M^{-2} s^{-1}) induced decay of ylide **3** correspond to an isotope effect of 4.3. In contrast, acetic acid facilitates decay of the 392 nm transient by a process which is first order in AcOH (3.1×10^8 M^{-1} s^{-1}) (Figure 4).

The chemical evidence accumulated in our studies of the photoreactions of *N*-phthaloyl α-amino acids[1b,d] suggests that azomethine ylides related to **4** (Scheme 1) serve as intermediates in these processes also. The results of LFP studies with the glycine derivative **2** corroborate this proposal. Pulsed irradiation

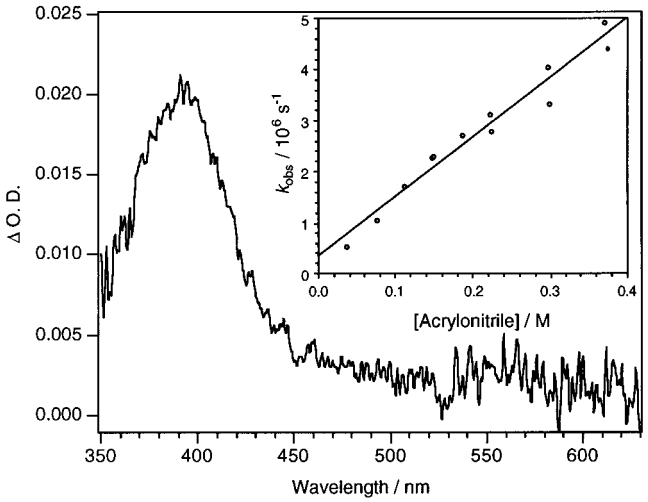


Figure 1. Transient absorption spectrum obtained (200 ns) following pulsed 266 nm irradiation of an N_2-saturated MeCN solution of **1** (5 mM) at 25 °C. The inset is a plot of the observed rate of decay monitored at 392 nm vs the concentration of acrylonitrile.

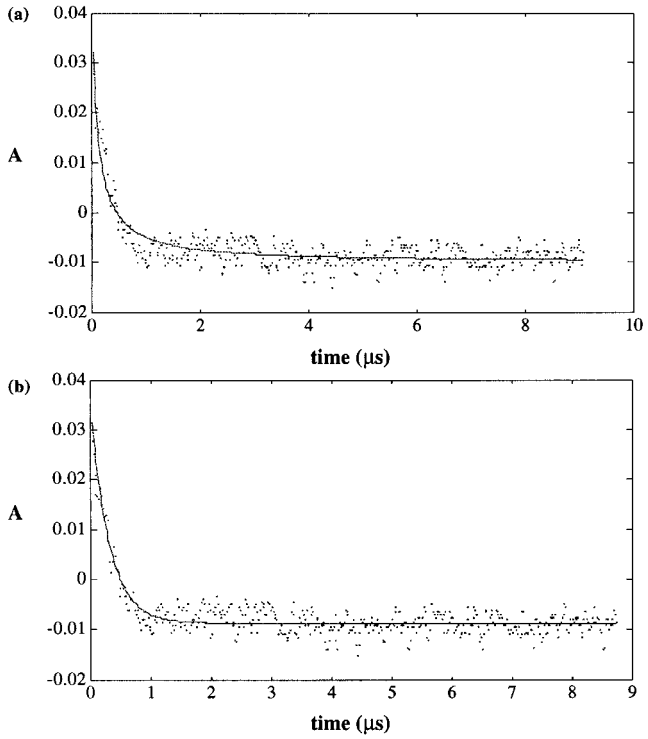


Figure 2. Experimental decay data (dots) for the 392 nm transient identified as ylide **3** arising by pulsed irradiation of (silylmethyl)-phthalimide **1** (solid lines) treated as a (a) first-order and (b) second-order decay process.

(308 nm) of **2** gives rise to a 392/345 nm absorbing transient whose decay profile is consistent with its assignment as the ylide **4**. Decay of **4** in MeCN follows first-order kinetics (2.9×10^6 s^{-1}) (Figure 5). The rate of decay of **4** is enhanced by the addition of MeOH (MeOD) in a manner which is first order in alcohol (2.8×10^5 M^{-1} s^{-1} for MeOH and 1.9×10^5 M^{-1} s^{-1} for MeOD, giving $k_{OH}/k_{OD} = 1.5$). Also, the rate of decay of this transient is enhanced by the addition of methyl acrylate, in a process which has a second-order rate constant of 2.7×10^7 M^{-1} s^{-1}.

It is difficult to obtain direct information about the nature of the excited state(s) that are responsible for the ylide-forming photoreaction of (silylmethyl)phthalimide **1** and glycine deriva-

(2) (a) Sato, Y.; Nakai, H.; Mizoguchi, T.; Kawanishi, M.; Hatanaka, Y.; Kanaoka, Y. *Chem. Pharm. Bull.* **1982**, *30*, 1263. (b) Griesbeck, A. G.; Henz, A.; Hirt, J.; Ptatschek, V.; Engel, T.; Loffler, D.; Schneider, F. W. *Tetrahedron* **1994**, *50*, 701. (c) Griesbeck (ref 2d) has also suggested that the photodecarboxylation reaction may involve excited-state proton transfer, which would be reasonable if singlets were the reactive excited states of these substrates. (d) Griesbeck, A. G.; Henx, A.; Peters, K.; Peters, E. M.; vonScnering, H. G. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 474.

Table 1. Spectroscopic and Kinetic Properties of Ylides Derived by Laser Flash Photolysis of Phthalimides **1** and **2**[a]

		rate constant			
phthalimide	transient (abs max)	no additive	methyl acrylate (acrylonitrile)	MeOH (MeOD)	AcOH
1	**3** (592 nm)	1.4×10^6 A^{-1} s^{-1}	8.9×10^6 M^{-1} s^{-1} (1.2×10^7 M^{-1} s^{-1})	1.9×10^5 M^{-2} s^{-1} (4.4×10^4 M^{-2} s^{-1})	3.1×10^8 M^{-1} s^{-1}
2	**4** (392, 345 nm)	2.9×10^6 s^{-1}	2.7×10^7 M^{-1} s^{-1}	2.8×10^5 M^{-1} s^{-1} (1.9×10^5 M^{-1} s^{-1})	

[a] Error limits for the decay rates in MeCN are estimated to be $\pm$ 0.1 $\times$ 10^6. The plots of k_{obs} vs additive concentrations gave r^2 values in the range of 0.94−0.99.4

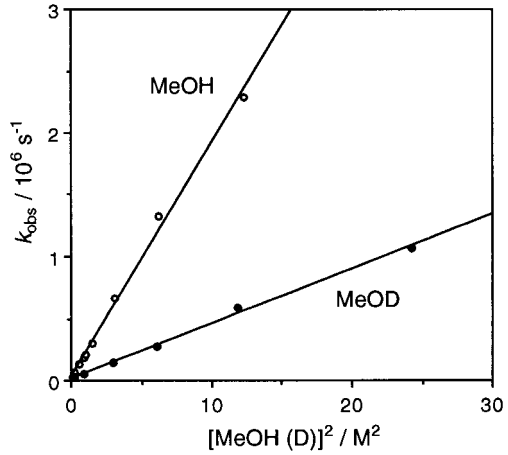


Figure 3. Observed rates of decay of the 392 nm transient (see Figure 1) formed by pulsed irradiation of **1** vs the squares of the concentrations of MeOH (empty circles) and MeOD (filled circles).

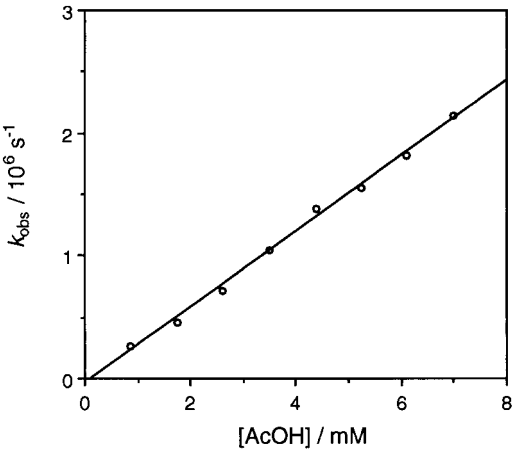


Figure 4. A plot of the observed rates of decay of the 392 nm transient (see Figure 1) formed by pulsed irradiation of **1** vs the concentration of acetic acid.

tive **2** owing to the weak or absent fluorescence emission of these and related *N*-alkylphthalimides.[3] In contrast, *N*-methyl-1,8- and -2,3-naphthalimide are known[3c] to efficiently fluoresce in fluid solution at 25 °C. In addition, we showed earlier[1b] that the (silylmethyl)-1,8-naphthalimide **9** also participates in photocycloaddition reactions with dipolarophiles, yielding the naphthoindolizidines **11** along with *N*-methyl-1,8-naphthalimide (**12**) (Scheme 2). In the current investigation, we found that irradiation of the related 2,3-naphthalimide in an MeCN solution containing 0.1 M acrylonitrile results in the formation of the pyrrolizidine **15** (Scheme 3). The stereochemical assignment

(3) (a) Although the fluorescence spectra and efficiencies of N- detect reliable fluorescence from *N*-methylphthalimide. (b) Coyle, J. D.: Harriman, A.; Newport, G. L. *J. Chem. Soc., Perkin Trans. 2* **1979**, 799. (c) Wintgens, V.; Valat, P.; Kossanyi, J.; Biczok, L.; Demeter, A.; Berces, T. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 411.

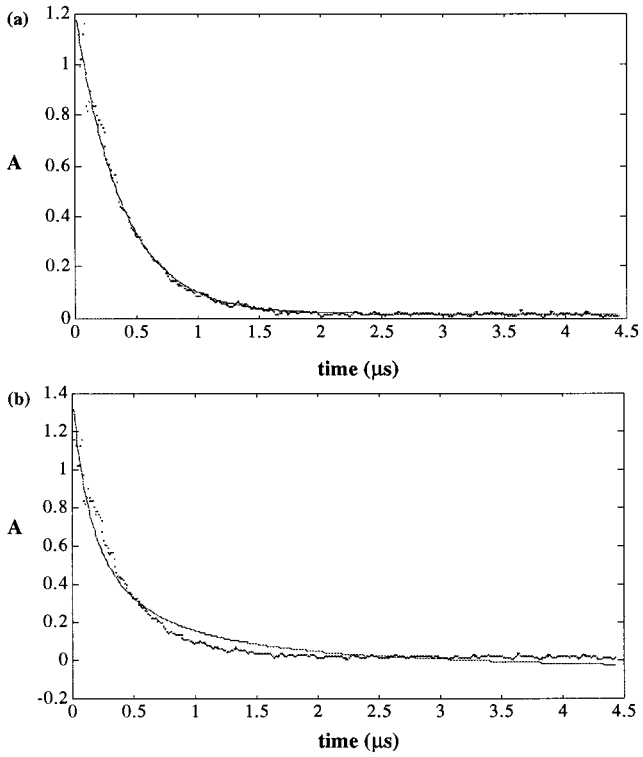
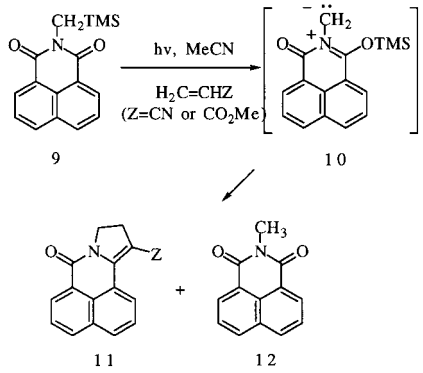


Figure 5. Experimental decay data (dots) for the 392 nm transient identified as ylide **4** arising by pulsed irradiation of *N*-phthaloylglycine **2** (solid lines) treated as a (a) first-order and (b) second-order decay process.

Scheme 2



to **15** is based on comparisons of ^{1}H and ^{13}C NMR data with those of closely related benzopyrrolizidines (e.g., **5**.[1b] Unlike the photoreactions of the simple *N*-(silylmethyl)phthalimide **1**, where cycloadduct **5** formation is the exclusive reaction pathway followed when dipolarophile concentrations are 0.1 M, the naphthalimides **9** and **13** react under these conditions to form adducts along with substantial amounts of the respective *N*-methyl derivatives **12** and **16**.

Scheme 3

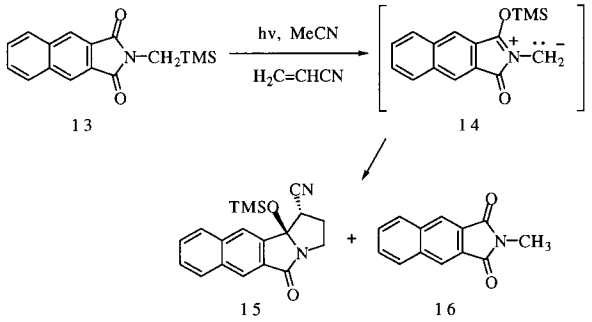
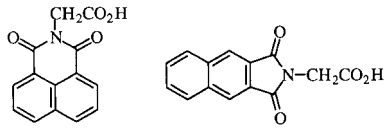


Table 2. Fluorescence Quantum Yields of *N*-CH_3, *N*-CH_2TMS, and *N*-CH_2CO_2H Naphthalimides in MeCN at 25 °C

naphthalimide (N-substituent)	$\lambda_{emission}$[a] (nm)	ϕ_f[b]
1,8-Naphthalimides		
9 (CH_2TMS)		0
12 (CH_3)	362, 378	0.02[c] (0.027)[d]
17 (CH_2CO_2H)	378	0.09
2,3-Naphthalimides		
13 (CH_2TMS)		0
16 (CH_3)	368, 380	0.3[c] (0.24)[d]
18 (CH_2CO_2H)	370, 378	0.4

[a] Excitation at 285 nm in all cases and substrate concentrations adjusted to ensure equal absorbance at this wavelength. [b] 2-Aminopyridine was used as the actinometer (ref 4) for these measurements.[c] This work. [d] Reference 3c.

To gain insight into the excited-state origin of the ylide-forming photoreactions, fluorescence measurements were made with the *N*-methyl-, -(silylmethyl)-, and -(carboxymethyl)-1,8- and -2,3-naphthalimides **9**, **12**, **13**, and **16**−**18**. The fluorescence



quantum yields of these substances in MeCN at 25 °C were determined by using 2-aminopyridine (λ_{excit} 285 nm, λ_{emiss} 367 nm, ϕ_f 0.6) as the actinometer.[4] The data, accumulated in Table 2, show that the placement of a TMS grouping into these naphthalimides results in complete quenching of their fluorescence. In contrast, the carboxylic acid analogues have larger fluorescence efficiencies compared to the corresponding *N*-methylnaphthalimides.

Additional information has been gained about the C-to-O silyl-migration reactivity of the triplet excited state of **1**. We observed that the 392 nm absorbing transient can also be generated by use of xanthone triplet-sensitized irradiation of the (silylmethyl)phthalimide. Pulse irradiation of a solution of **1** and xanthone leads to initial formation of the xanthone triplet absorbing at 620 nm. This transient is quenched by **1** at a near-diffusion-controlled rate (6.8×10^9 M^{-1} s^{-1}) with concomitant formation of the 392 nm transient assigned to ylide **3**.

Discussion

Azomethine Ylide Formation. The interpretations given to the data presented above are based on the proposition that the 392 nm absorbing transients arising by photolysis of phthalimide derivatives **1** and **2** correspond to the respective azomethine ylides **3** and **4**. Although absorption spectra of a variety of azomethine ylides have been recorded,[5] spectroscopic data are not available for ylides which have the structural features and substitution patterns found in **3** and **4**. Concern that the transients ascribed to these ylides might really be the triplets of **1** and **2** was alleviated by comparing the data accumulated in this study with those reported for *N*-alkylphthalimides by Coyle[3b] and Wintgens.[3c] These workers have shown that the triplets of *N*-methylphthalimide and its homologues have (1) absorption maxima at 320−340 nm, (2) first-order decay profiles, and (3) decay rates which increase by 4-fold in changing the solvent from cyclohexane to methanol. These data differ dramatically from those found in our studies with the phthalimides **1** and **2**.

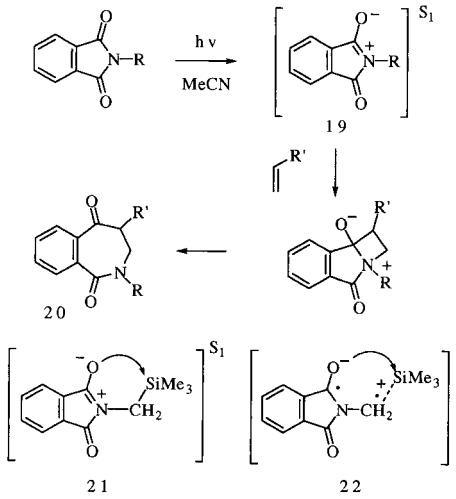
Additional information which is relevant to this issue has come from transient quenching studies. We observed that photolysis of phthalimide and its *N*-methyl derivative gives rise to transients absorbing at 336 and 337 nm, respectively, and that these species are quenched at a diffusion-controlled rate ($(1.8-2.0) \times 10^{10}$ M^{-1} s^{-1}) by ferrocene, a known[6] triplet (ca. 38 kcal/mol) quencher. Also, the rates of decay of the 336 and 337 nm transients are not affected by acetic acid (0.1 M). In contrast, the 392 nm absorbing transient arising by irradiation of the (silylmethyl)phthalimide **1** is not quenched by ferrocene, and as described above, its decay rate is greatly facilitated by the addition of acetic acid. Thus, the accumulated data provide strong support for the assignments of the 392 nm absorbing tansients as the azomethine ylides **3** and **4**.

The results of this study confirm our earlier proposal that azomethine ylides serve as key intermediates in photoreactions of (silylmethyl)phthalimides and phthalimide derivatives of α-amino acids. The effort has also unveiled additional information about the ylide-forming excited-state processes. On the basis of the fluorescence quantum yield data given in Table 2, it appears that *N*-(silylmethyl)naphthalimide (and perhaps phthalimide) singlet excited states are involved in the direct irradiation-promoted C-to-O silyl-migration reactions that produce the OTMS-substituted azomethine ylides. This proposal is consistent with the observation that the singlet-state fluorescence of the naphthalimides is completely quenched by introduction of the *N*-CH_2TMS moiety. However, the observation that the triplet (74 kcal/mol) can sensitize the formation of the OTMS-ylide **3** demonstrates that the triplet state of **1** also participates in the silyl-migration process.

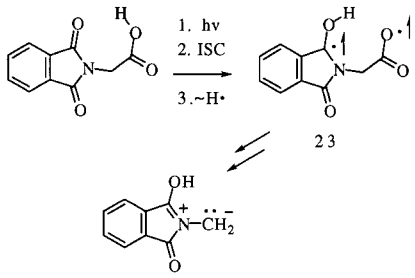
The driving force for the ylide-forming silyl-rearrangement process can be thought about in several ways. It is well-known[3] that phthalimides participate in 2+2-type photocycloaddition reactions with non-electron-rich alkenes to form benzazepindione products **20** (Scheme 4). These results suggest that the dipolar structure **19** is a reasonable contributor to the singlet excited states of these substrates. As such, it is possible to envisage the ylide-forming reaction of singlet states **21** of *N*-(silylmethyl)phthalimides as a rearrangement involving transfer of the silyl group to the silophilic oxyanion carbonyl oxygen center from the more weakly bonded C−Si position. Relevant to this are the observations made by Vedejs[8] and Padwa,[9] which show that *N*-(silylmethyl)iminium salts undergo facile desilylation to produce azomethine ylides.

(4) Rusakowicz, R.; Testa, A. C. *J. Chem. Phys.* **1968**, *21*, 2680.
(5) Das, P. K. In *Handbook of Organic Photochemistry*; Scaiano, J. C., Ed.; CRC Press: Boca Raton, FL, 1989; Vol. II, pp 35−70.
(6) Farmillo, A.; Wilkinson, F. *Chem. Phys. Lett.* **1975**, *34*, 575.
(7) (a) Maruyama, K.; Kubo, Y. *J. Org. Chem.* **1981**, *46*, 3612. (b) Mazzochi, P. M.; Bowen, M. J.; Narain, N. K. *J. Am. Chem. Soc.* **1977**, *99*, 7063.
(8) Vedejs, E.; Martinez, G. R. *J. Am. Chem. Soc.* **1979**, *101*, 6542.
(9) Padwa, A.; Haffmans, G.; Tomas, M. *Tetrahedron. Lett.* **1983**, *24*, 4303.

Scheme 4



Scheme 5



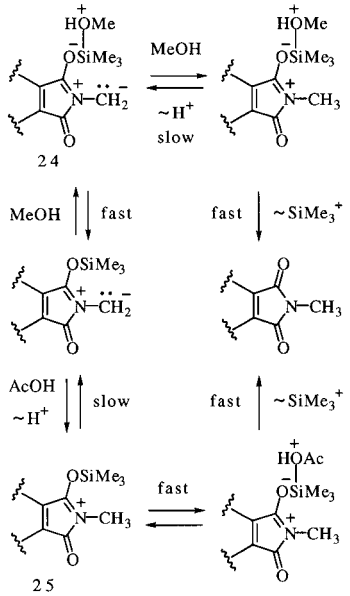
Alternatively, the singlet and triplet excited-state silyl-transfer processes might be driven by intramolecular electron transfer from the σ_{C-Si} donor to the high-energy phthalimide singlet or triplet excited states. From this perspective, C-to-O silyl migration would occur in the short-lived zwitterionic diradical **22**. Support for this proposal is found in our recent studies with (silylalkyl)phthalimides,[10] in which we have found that facile intramolecular SET from σ_{C-Si} donor sites to phthalimide excited singlets promotes silyl transfer to silophiles such as water.

The emission data presented in Table 2 show that the presence of a carboxylic acid function in the *N*-naphthoylglycines **17** and **18** leads to a slight enhancement of the fluorescence efficiencies. This phenomenon might be due to intramolecular hydrogen-bonding between the side chain carboxyl and imide carbonyl groups and its effect on the energetic ordering of naphthalimide n−π* vs $\pi-\pi$* singlet excited states. Hydrogen-bonding interactions should also exist in related *N*-phthaloylglycine derivatives.[11] Importantly, the fluorescence data show that the presence of carboxylic acid side chains in the naphthalimides **17** and **18** does not bring about singlet-state quenching. This observation is consistent with the findings of Kanaoka[2a] and Griesbeck[2b,c] which suggest that photodecarboxylation reactions of *N*-phthaloyl α-amino acids are initiated by triplet excited-state H-atom abstraction followed by rapid decarboxylation of the formed carboxy radicals **23** (Scheme 5). Intersystem crossing needed to reenter the ground-state singlet ylide manifold can occur at any stage following diradical **23** formation and decarboxylation.

(10) Lee, Y. J.; Ling, R,; Mariano, P. S.; Yoon, U. C.; Kim, D. U.; Oh, S. W. *J. Org. Chem.* **1996**, *61*, 3304.

(11) For a general review see: Turro, N. J. *Modern Molecular Photochemistry*; Benjamin-Cummings: Menlo Park, CA, 1978; pp 41−43 and 165−70. For the specific example of fluorenone see: Caldwell, R. A.; Gajewski, R. P. *J. Am. Chem. Soc.* **1971**, *93*, 532 and references therin.

Scheme 6

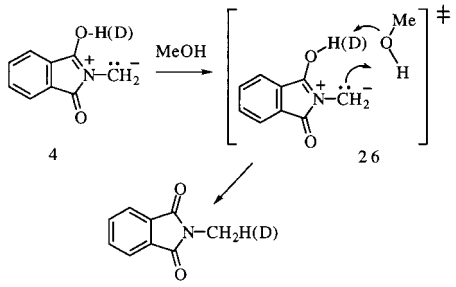


Azomethine Ylide Reactions. Product distribution and reaction quantum yield data accumulated in our earlier studies[1b] suggest that the major pathways for the decay of azomethine ylides, formed by irradiation of *N*-(silylmethyl)phthalimides, involve protodesilylation to form *N*-methylphthalimides and dipolar cycloaddition with dipolarophiles to form benzopyrrolizidines. Aziridine-forming electrocyclic ring closure, a common reaction open to azomethine ylides derived by photolysis of aziridines[12] and acyclic *N*-(silylmethyl)imides,[1c] is not a major process responsible for the decay of phthalimide-derived ylides as judged by the absence of ring expansion products in the preparative photoreaction mixtures. The kinetic data also show that a, by necessity slow, bimolecular pathway is also involved in the decay of these intermediates. Information is not currently available to offer a hint at the mechanism for this interesting bimolecular decay process.

The results of our earlier chemical and current LFP studies demonstrate that the decay of (silylmethyl)phthalimide-derived ylide is enhanced by methanol and acetic acid owing to reactions that lead to the production of *N*-methylphthalimides. The differences between the molecularity of these protodesilylation reactions with MeOH vs AcOH suggest the operation of two different, but perhaps related, mechanisms. A two-step route (Scheme 6, top) involving preequilibrium formation of the silylate complex **24** best explains the kinetic order and large (4.3) OD-isotope effect associated with MeOH-promoted decay of ylide **3**. Collapse of **24** by proton transfer from MeOH is expected to be rate limiting in this case owing to the high silophilicity and low acidity of this alcohol. A similar mechanism might be responsible for acetic acid-promoted decay of the OTMS-azomethine ylide intermediate. In this case, addition of AcOH to form a silylate complex analogous to **24** should be rate limiting (i.e., protonation of the silylate complex by AcOH should be fast). Consequently, the reaction would be, as is observed, first order in AcOH. Alternatively, the ordering of the protonation and desilylation steps might be reversed in the AcOH-induced decay process. In this route (Scheme 6, bottom), the first step would be reversible AcOH-promoted C-protonation to form intermediate iminium salts **25**. Deprotonation of **25** by acetate should be slow relative to desilylation. Thus, the first

(12) Hermann, H.; Huisgen, R.; Mader, H. *J. Am. Chem. Soc.* **1971**, *93*, 1779; Padwa, A.; Hamilton, A. *J. Heterocycl. Chem.* **1967**, *4*, 118.

Scheme 7



step in this process would be rate limiting, and therefore, the overall reaction would be first order in AcOH.

The OH-azomethine ylides formed by irradiation of *N*-phthaloyl α-amino acids are readily transformed to *N*-methylphthalimides by intramolecular proton transfer. Interestingly, MeOH plays a catalytic role by serving to enhance the rate of this reaction. The first-order MeOH involvement and small (1.5) OD-isotope effect associated with enhanced decay of ylide **4** suggest that MeOH may simply act as a bridge (e.g., **26**) in the proton-transfer relay (Scheme 7). The small OD-isotope effect associated with the MeOH- vs MeOD-promoted decay of the OH- vs OD-ylide **4** might also be a consequence of the slower rate of intramolecular D vs H transfer, leading to the *N*-deuteriomethyl vs *N*-methyl product.

The LFP results have clarified several observations made in our earlier studies[1] of the preparative photochemistry of the azomethine ylide precursors. Specifically, we found that irradiation of the *N*-(silylmethyl)phthalimide (**1**) in MeCN solutions containing 0.1 M methyl acrylate leads to exclusive and high-yielding formation of the cycloadduct **5** (Scheme 1). Under these conditions, none of the *N*-methylphthalimide (**8**) is formed. In contrast, reactions of the *N*-phthaloyl α-amino acids such as the glycine derivative **2** in MeCN with 0.1 M methyl acrylate lead to lower yielding production of the cycloadducts along with commensurate generation of *N*-methyl products.[1] We now know that one reason for the differences in the reactivity profiles of the OTMS- and OH-ylides **3** and **4** is that the latter intermediate undergoes rapid (2.9×10^6 s^{-1}) unimolecular 1,4-hydrogen transfer to produce the *N*-methyl product in competition with bimolecular dipolar cycloaddition with methyl acrylate (2.7×10^7 s^{-1} M^{-1}). In contrast, the decay of the OTMS ylide **3**, owing to its bimolecular nature, is slow relative to cycloadditions with dipolarophiles.

Summary. The studies described above have led to a clearer understanding of the mechanisms for azomethine ylide formation and decay in the photochemistry of *N*-(silylmethyl)phthalimides and *N*-phthaloyl α-amino acids. With the detailed knowledge provided by these efforts, we are better positioned to design synthetically relevant photoreactions of these substrates.

Experimental Section

General Procedures. All reported reactions were run under a dried nitrogen atmosphere. Unless otherwise noted, all reagents were obtained from commercial sources and used without further purification. All compounds were isolated as oils and shown to be >90% pure by ^{1}H and/or ^{13}C NMR unless otherwise noted.

^{1}H NMR and ^{13}C NMR spectra were recorded by using $CDCl_3$ solutions unless otherwise specified and chemical shifts are reported in parts per million relative to residual $CHCl_3$ at 7.24 ppm (for ^{1}H NMR) and 77.0 ppm (for ^{13}C NMR). ^{13}C NMR resonance assignments were aided by the use of the DEPT technique to determine numbers of attached hydrogens, and ^{1}H NMR coupling constants (*J*-values) are reported in hertz. Infrared data are reported in units of inverse centimeters. Low (MS) and high (HRMS) resolution mass spectra, reported as *m*/*z* (relative intensity), were recorded by using electron impact ionization (EI).

Photochemical reactions were conducted by using an apparatus consisting of a 450 W medium-pressure mercury lamp surrounded by a glass filter and within a quartz, water-cooled well that was purged with O_2-free N_2 both before and during irradiation. Photochemical reaction progress was monitored by TLC or ^{1}H NMR.

Laser Flash Photolysis Experiments. Nitrogen-saturated MeCN solutions of **1** and **2** at 25 °C were subjected to pulse irradiation by using either the fourth (266 nm) harmonic output from a Q-switched Nd:YAG laser (6−8 ns pulse width) or an XeCl (308 nm) excimer laser (6−10 ns pulse). The probe assembly for measurement of time-resolved spectra consists of either a 150 W xenon lamp and a polychromator equipped with an image intensifier coupled with an image sensor or a 450 W xenon lamp and a digital oscilloscope.

***N*-[(Trimethylsilyl)methyl]-2,3-naphthalimide (13).** A suspension of 0.18 g (4.6 mmol) of NaH (60% dispersion) and 2,3-naphthalimide (0.3 g, 1.5 mmol) in 5 mL of DMF was stirred for 20 min at 0 °C, and 0.90 g (4.56 mmol) of (trimethylsilyl)methyl iodide was added. The mixture was stirred for 12 h at 25 °C, diluted with water, and extracted with ether. The ethereal extracts were dried and concentrated in vacuo, giving a residue which was subjected to silica gel chromatography (hexane−diethyl ether), giving 0.3 g (75%) of **13**: mp 128−129 °C (hexane); ^{1}H NMR δ 8.19 (2H, s, ArH), 7.93 (2H, m, ArH), 7.59 (2H, m, ArH), 3.21 (2H, s, CH_2), 0.06 (9H, s, TMS); ^{13}C NMR δ 168.1 (CO), 135.3 (C), 130.2 (CH), 129.0 (CH), 128.1 (C), 124.1 (CH), 29.5 (CH_2), −1.8 (TMS); IR ($CHCl_3$) 1760, 1694, 1640, 1605 cm^{-1}; UV (MeCN) 259 (113 000), 358 (7800) nm; EIMS *m*/*z* (rel intens) 283 (M^+, 48), 282 (100), 268 (56), 74 (49); HRMS *m*/*z* 283.1016 ($C_{16}H_{17}NO_2Si$ requires 283.1028).

Photochemistry of *N*-[(Trimethylsilyl)methyl]-2,3-naphthalimide (13). An N_2-purged solution of **13** (220 mg, 0.78 mmol) and 0.7 mL (10.5 mmol) of acrylonitrile at 25 °C in 110 mL of MeCN was irradiated using Pyrex-filtered light for 22 h (100% conversion). The photolyzate was concentrated in vacuo, giving a residue which was subjected to chromatography on silica gel (hexanes−ether) to give 17 mg (10%) of **15**, 4 mg (3%) of 2,3-naphthalimide, and 34 mg (14%) of the known[12] phthalimide **16** (hexane−ether).

Data for 15: mp 177−178 °C; ^{1}H NMR δ 8.26 (1H, s, ArH), 7.97 (1H, s, ArH), 7.91 (2H, d, J = 7.9, ArH), 7.56 (2H, d, J = 7.9, ArH), 3.95 (1H, dd, J = 9.4, J = 9.1, CHN), 3.51 (1H, t, CHN, J = 9.4), 3.42 (1H, d, J = 6.6, CHCN), 2.85 (1H, m, CH_2), 2.61 (1H, m,CH_2), −0.18 (9H, s, TMS); ^{13}C NMR δ 169.4 (CO), 139.2 (C), 135.6 (C), 134.2 (C), 130.0 (CH), 129.8 (CH), 128.7 (CH), 128.4 (CH), 127.4 (CH), 124.8 (CH), 122.7 (CH), 117.4 (CN), 98.0 (C−OTMS), 41.1 (CH_2), 40.2 (CH), 32.1 (CH_2), 0.6 (TMS); IR ($CHCl_3$) 2361 (CN), 1714 (CO) cm^{-1}; EIMS *m*/*z* (rel intens) 336 (M^+, 24), 283 (54), 282 (100); HRMS *m*/*z* 336.1290 ($C_{19}H_{20}N_2O_2Si$ requires 336.1293).

***N*-(Carbomethoxymethyl)-1,8-naphthalimide (17).** A suspension of 0.6 g (0.015 mol) of NaH (60% dispersion) and 1,8-naphthalimide (1.0 g, 0.01 mol) in 5 mL of DMF at 0 °C was stirred for 20 min. After addition of 1.6 mL (0.015 mol) of ethyl bromoacetate the mixture was stirred for 12 h at 25 °C, diluted with water, and extracted with ether. The ethereal extracts were dried and concentrated in vacuo, giving 1.4 g (98%) of *N*-(carbomethoxymethyl)-1,8-naphthalimide (**17**): mp 162−163 °C (hexane−ether); ^{1}H NMR δ 8.61 (2H, d, J = 7, ArH), 8.23 (2H, d, J = 8.1, ArH), 7.76 (2H, t, J = 7.0, ArH), 4.95 (2H, s, CH_2), 4.25 (2H, q, J = 7.0, CH_2), 1.30 (3H, t, J = 7.0, CH_3); ^{13}C NMR δ 168.1 (CO), 163.8 (CO), 134.3 (ArH), 132.6 (ArH), 131.6 (ArH), 128.3 (C), 126.9 (ArH), 122.2 (C), 61.6 (CH_2), 41.4 (CH_2), 14.1 (CH_3); IR ($CHCl_3$) 1746, 1700, 1663 cm^{-1}; EIMS *m*/*z* (rel intens) 283 (M^+, 32), 210 (100); HRMS (EI) *m*/*z* 283.0839 ($C_{16}H_{13}NO_4$ requires 283.0844).

A suspension of 1.0 g (3.5 mmol) of this ester in 30 mL of 15% aqueous HCl was stirred at reflux for 6 h and concentrated in vacuo, giving 0.88 g (97%) of **17**: mp 250 °C dec (acetone−ether); ^{1}H NMR (acetone-d_6) δ 8.56 (2H, d, J = 7.2, ArH), 8.43 (2H, d, J = 8.6, ArH), 7.86 (2H, t, J = 7.2, ArH), 4.87 (2H, s, CH_2); ^{13}C NMR (acetone-d_6) δ 169.3 (CO), 164.1 (CO), 135.3 (CH), 132.7 (C), 131.72 (CH), 128.8

(13) Rigaudy, J.; Sparfield, D. *Tetrahedron* **1978**, *39*, 2263.

(C), 127.9 (CH), 121.0 (C), 41.4 (CH_2); IR ($CHCl_3$) 3300, 1720, 1651, 1644 cm^{-1}; UV (MeCN) 218 (46 000), 318 (13 600), 335 (11 100) nm; EIMS *m*/*z* (rel intens) 255 (M^+, 10), 211 (100), 210 (57); HRMS (EI) *m*/*z* 255.0534 ($C_{14}H_9NO_4$ requires 255.0531).

***N*-(Carboxymethyl)-2,3-naphthalimide (18).** A solution of glycine (0.49 g, 6.67 mmol), 2,3-naphthalic anhydride (1.2 g, 6.05 mmol), and 30 mL of triethylamine in 30 mL of xylene was stirred at reflux with azeotropic removal of water for 15 h and concentrated in vacuo, giving a solution which was acidified with 10% aqueous HCl. The solid obtained was filtered, washed with water, and dried, giving 1.36 g (88%) of **18**: mp 240 °C dec (acetone−ether); ^{1}H NMR (acetone-d_6) δ 8.46 (2H, s, ArH), 8.05 (2H, m, ArH), 7.77 (2H, m, ArH), 4.45 (2H, s, CH_2); ^{13}C NMR (acetone-d_6) δ 168.8 (CO), 167.6 (CO), 136.5 (C), 131.2 (CH), 130.26 (CH), 128.8 (C), 125.6 (CH), 39.4 (CH_2); IR ($CHCl_3$) 1736, 1713 cm^{-1}; UV (MeCN) 258 (59 800), 358 (6000) nm; EIMS *m*/*z* (rel intensity) 255 (M^+, 23), 211 (81), 210 (100); HRMS *m*/*z* 255.0538 ($C_{14}H_9NO_4$ requires 255.0531).

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Supporting Information Available: Spectroscopic data in the form of ^{1}H and ^{13}C NMR spectra for all previously unreported compounds (**13, 15**, **17**, and **18**) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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