

Dipole-Forming Photochemical Group Transfer Reactions of Phthalimides and α -Ketoamides

Ung Chan Yoon*¹ and Patrick S. Mariano²

¹Department of Chemistry and Chemistry Institute for Functional Materials
Pusan National University, Busan 609-735, Korea

²Department of Chemistry, University of New Mexico,
Albuquerque, New Mexico 87131, USA

Results of studies of SET-promoted dipole-forming photochemical group transfer reactions of phthalimide and α -ketoamide derivatives are discussed. Azomethine ylide forming photochemical reactions, which are initiated by intramolecular SET from tethered silylmethyl-, carboxymethyl-, and β -hydroxyethyl containing electron donors to excited states of phthalimides, related maleimides, and conjugated imides, are presented first. Following this, investigations of regioselective 1,4-dipole forming photochemical reactions of N-trialkylsilylmethyl- and N-trialkylstannyl- α -ketoamides are described.

Key words: azomethine ylide, 1,4-dipole formation, SET-promoted photoreactions, N-silyl-phthalimides, N-stannyl- α -ketoamides

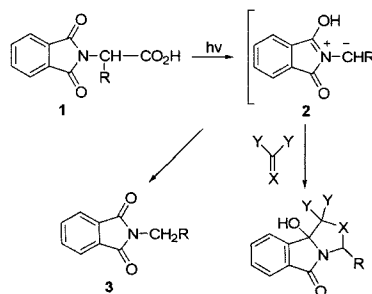
INTRODUCTION

Past studies have shown that phthalimides participate in a number of mechanistically interesting photochemical processes [1-2]. For example, like their ketone counterparts phthalimide singlet and triplet excited states have been found to undergo both intermolecular and intramolecular H-atom abstraction reactions [3-6]. The intramolecular process is analogous to Norrish type-II reactions of ketones in that it displays the typical preference for H-atom abstraction at the γ -position. Thus, as is the case with other carbonyl compounds [7], the excited states of these substances have oxy-radical character.

In addition, electronic 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 [8-14]. Also, phthalimides in their singlet excited states undergo photochemical cycloaddition reactions with non-electron donating olefins, which result in the formation of benzazepindione products [15-16]. Their participation in this cycloaddition process suggests that phthalimide singlet excited states have a large C-N π -bond order.

Our interest in this well-studied area of photochemistry was initially stimulated by the congruence of thoughts about a number of issues related to phthalimide excited state reactivity. The first concerns questions about the potential

SET-promoted photochemical reactivity of N-(silylalkyl) phthalimides. It has been reported that alkylsilanes undergo photoaddition reactions with electron acceptors (*e.g.*, polycyanoarenes) which are driven by SET from σ_{C-Si} bonds [17]. In recent studies [18, 19], we observed photochemical reactions of this type with 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 dissociation energy difference would facilitate processes in which a silyl group of an alkylsilanes is transferred to an oxy radical with concomitant hemolytic formation of a O-Si bond and cleavage of a C-Si bond (*i.e.*, S_{H2} ~ reactions) [20-23]. Finally, the enhanced C-N π -bond order [15, 16] responsible for cycloaddition reactivity, suggests that phthalimide singlet excited states have zwitterionic character with negative and positive charge densities at 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 trialkylsilyl cation transfer.



Scheme 1.

*To whom correspondence should be addressed.

E-mail : ucyoon@pusan.ac.kr

Received Dec. 12, 2005 Accepted Dec. 27, 2005

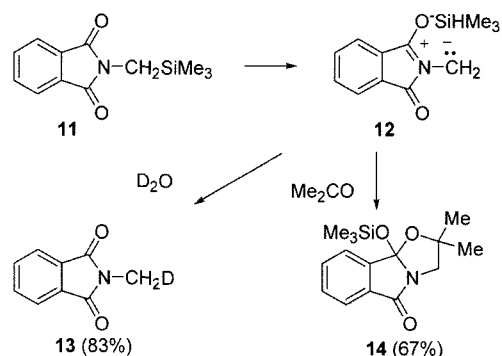
Another interesting excited-state reaction, discovered by Kanaoka and his co-workers several years ago, is photodecarboxylation of *N*-phthalimido- α -amino acids (**1**, Scheme 1) [24]. This process proceeds via the intermediacy of azomethine ylides **2**. More recently, we showed that the ylide intermediates **2** can be trapped by cycloaddition reactions with carbonyl and alkene dipolarophiles [25-28]. In addition, the results of parallel laser flash photolysis (LFP) investigations provided evidence for the existence of azomethine ylides as intermediates in *N*-phthalimido- α -amino acid photoreactions and rate data for their cycloaddition and intramolecular proton-transfer reactions [29].

Azomethine Ylide-Forming Photoreactions of *N*-(Trimethylsilyl-methyl)phthalimides

An evaluation of observations made in studies of phthalimide photochemistry led to the prediction that *N*-(silylmethyl)phthalimides **4** might display unique and interesting photochemical reactivity. We anticipated that excited states of these substances could react to produce novel azomethine ylides **8-9** by pathways involving SET and subsequent desilylation of σ_{C-Si} cation radicals (Scheme 2).

In this case, the zwitterionic biradicals **5** generated by SET in the triplet or singlet excited states of **4** could undergo nucleophile-induced desilylation to form 1,3-biradicals **6** (if triplets) or azomethine ylides **8** (if singlets). Alternatively, the oxyanion center in **5** could serve as an internal nucleophile promoting trimethylsilyl transfer from carbon to oxygen in **5**. This process, being both energetically and entropically favored, would result in production of the silicon containing biradical or dipolar intermediates, **7** or **9**. Cyclizations of **6-9** would generate strained bicyclaziridines **10**. Consequently, we anticipated that these transients would be long-lived and, thus, capable of reacting with trapping agents (Scheme 2).

Observations made in studies with the parent (silylmethyl)phthalimide **11** confirmed the operation of this unique excited-state process involving sequential SET-silyl transfer [25-27]. We found that irradiation of **11** in D_2O -MeCN results in efficient production of monodeuteriated *N*-methylphthalimide **13**, while excited-state reaction of this phthalimide in acetone gives rise to the cycloadduct **14** (Scheme 3). The intermediate

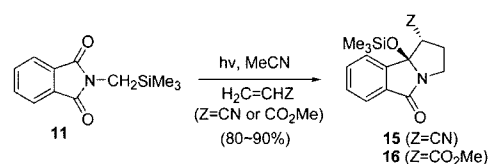


Scheme 3.

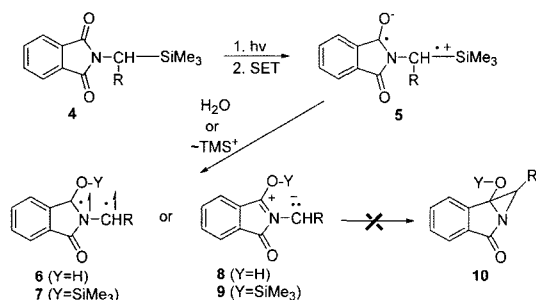
in these processes is the azomethine ylide **12**, which reacts by C-deuteration with D_2O or dipolar cycloaddition with acetone to form **13** and **14**, respectively.

LFP techniques were used to gain evidence for the intermediacy of azomethine ylides in these processes [29]. Excitation (266 nm) of **11** in MeCN gives rise to a 392-nm-absorbing transient which undergoes second-order decay ($1.4 \times 10^6 A^{-1} s^{-1}$). Added dipolarophiles, e.g., methyl acrylate and acrylonitrile, enhance the decay of the 392 nm transient, with second-order rate constants around $1 \times 10^7 M^{-1} s^{-1}$. The results are in accord with the assignment of the 392 nm-absorbing transient as azomethine ylide **12** and the bimolecular decay pathways promoted by methyl acrylate and acrylonitrile as dipolar cycloaddition processes.

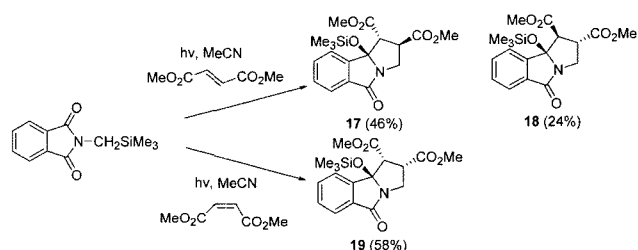
Preparative photochemical investigations provided supporting evidence for this proposal [25, 26]. Irradiation of **11** in MeCN solutions containing 10 mM acrylonitrile or methyl acrylate leads to efficient (80-90%) formation of the respective benzopyrrolizidines **15** and **16** (Scheme 4). The ylide trapping reactions are endo-selective and stereospecific (preferential production of **17** + **18** and **19** from photoreactions of **11** with dimethyl fumarate and dimethyl maleate, respectively) (Scheme 5).



Scheme 4.



Scheme 2.

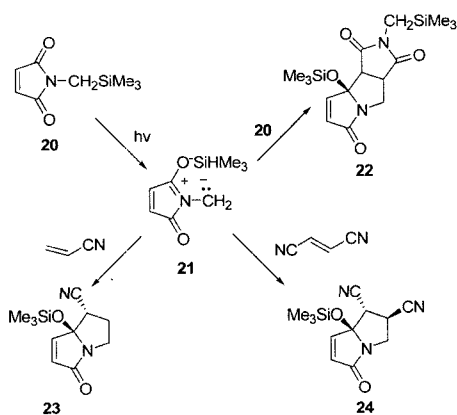


Scheme 5.

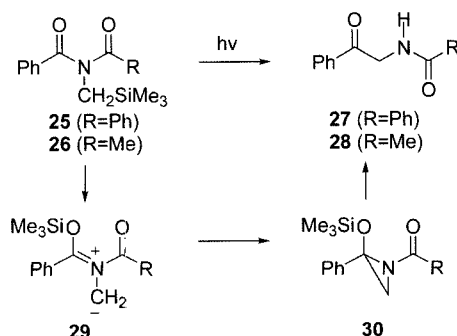
Azomethine Ylide-Forming Photoreactions of *N*-(Trimethylsilylmethyl)-Substituted Conjugate Imides

The novel and preparatively useful azomethine ylide forming photoreaction is not restricted to phthalimide substrates [27]. Other conjugated imides that contain *N*-silylmethyl substitution are transformed to their corresponding azomethine ylides by a photoinduced C-to-O silyl migration process. For example, irradiation of *N*-(trimethylsilylmethyl) maleimide **20** in MeCN results in efficient formation of the adduct **22** (Scheme 6) arising from self-trapping of the intermediate ylide **21**. This intermediate is competitively trapped by cycloaddition with added dipolarophiles such as acrylonitrile (\rightarrow **23**) and fumaronitrile (\rightarrow **24**).

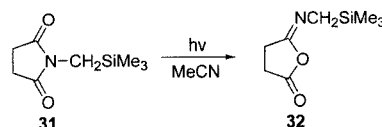
Azomethine ylide formation also occurs from the excited states of symmetric and unsymmetric benzimides **25** and **26** (Scheme 7) [27]. Irradiation of these substrates in MeCN leads to generation of the respective α -amido ketones **27** and **28**. In the chain extension processes, excited-state C-to-O silyl migration is followed by 4π -electrocyclization of the formed ylide **29**. The unstable, aziridinyl ethers **30** formed in this manner can be detected by ^1H NMR monitoring of photoreactions conducted under rigorously anhydrous conditions. Desilylative ring opening then occurs on exposure



Scheme 6.



Scheme 7.



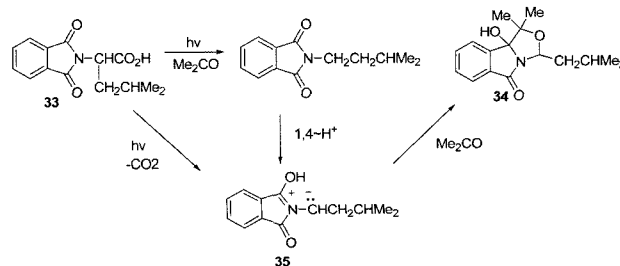
Scheme 8.

of these substances to water, yielding the amido ketone products. Interestingly, the acyclic azomethine ylides **29** are not trapped by even high concentrations of highly reactive dipolarophiles, e.g., fumaronitrile.

In contrast to phthalimide and conjugated imide analogues, *N*-trimethylsilylmethyl derivatives of simple, nonconjugated imides, as well as *N*-trimethylsilylmethyl amides, do not participate in excited-state C-to-O silyl migration reactions. An example is found in the photochemistry of the *N*-(silylmethyl)succinimide **31**, where irradiation promotes a well-known acyl migration to produce the unstable imide derivative **32** (Scheme 8) [30]. Observations made in these studies suggest that the novel C-to-O silyl migration reaction of conjugated imides is a general excited-state process. It is reasonable to propose that these reactions occur in imides that have low-energy π - π^* singlet or triplet excited states. As suggested above, the driving force for silyl migration could reside in both the respective redox potentials of the conjugated imide acceptor and $\sigma_{\text{C-Si}}$ donor sites and the entropic favorability of silyl transfer in the intermediate zwitterionic biradicals. In the case of nonconjugated imide counterparts, low-energy n - π^* states exist, and these react through acyl cleavage rather than SET pathways.

Ylide-Forming Photoreactions of *N*-Phthaloyl- α -Amino Acid and *N*-Phthaloyl- β -Amino Alcohols

As mentioned above, Kanaoka and his coworkers [24] reported that *N*-phthaloyl- α -amino acids **1** undergo high yielding photodecarboxylation reactions to produce the corresponding *N*-alkylphthalimides **3** (Scheme 1). The existence of azomethine ylides **2** as intermediates in these excited-state processes is hinted at by Kanaoka's observation that adduct **34** is formed as a minor product when *N*-phthaloyl-leucine **33** is irradiated in acetone (Scheme 9). We felt that **34** might



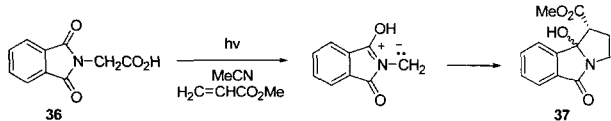
Scheme 9.

arise in this process by dipolar cycloaddition of acetone to the ylide **35** in competition with its decay by proton transfer (\rightarrow **33**). The former process is reminiscent of the acetone cycloaddition reaction of the (silylmethyl)phthalimide-derived azomethine ylide **12** (see Scheme 3).

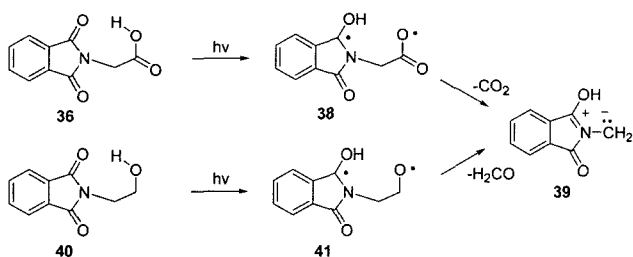
Mechanistic and exploratory investigations in our laboratories have demonstrated that azomethine ylides definitely are intermediates in *N*-phthaloyl- α -amino acid photodecarboxylation reactions. Evidence for this conclusion comes in part from the results of laser flash photolysis studies of *N*-phthaloyl-glycine [29]. Flash excitation of this substance gives rise to a 392-nm-absorbing transient characterized as the HO ylide (Scheme 10). Like its similarly absorbing (silylmethyl)phthalimide-derived, TMSO counterpart, this transient undergoes methyl acrylate- or acrylonitrile-induced decay with second-order rate constants around $3 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$. In addition, irradiation of *N*-phthaloyl-glycine **36**, as well as other phthalimido- α -amino acid derivatives, in MeCN solutions containing the dipolarophiles, methylacrylate and acrylonitrile results in clean formation of benzopyrrolizidine adducts (e.g., **37**) [29].

The transformation of *N*-phthaloyl- α -amino acids to azomethine ylides could be initiated by hydrogen atom abstraction. Transfer of the carboxylic acid hydrogen to the excited phthalimide carbonyl oxygen would generate the carboxy radical containing diradical **38**, a direct precursor of the azomethine ylide intermediate **39** (Scheme 11). *N*-Phthaloyl derivatives of β -amino alcohols **40** participate in a very similar hydrogen atom transfer reaction to produce biradicals **41**, which serve as precursors of azomethine ylides **39** [28]. In both cases, azomethine ylide production occurs by way of a homolytic C-C bond-cleaving processes (Scheme 11). The conversion of the phthalimido-alcohol **42** to benzaldehyde, phthalimide, and benzopyrrolizidine **43** by irradiation in an

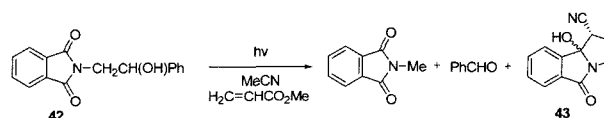
The conversion of the phthalimido-alcohol **42** to benzaldehyde, phthalimide and benzopyrrolizidine **43** by



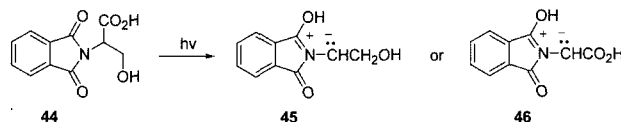
Scheme 10.



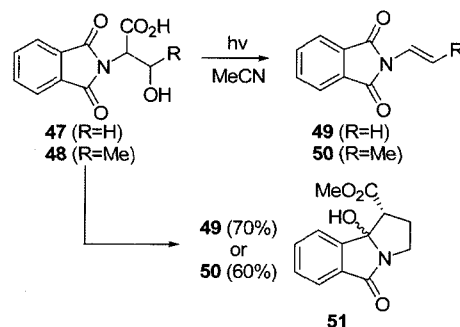
Scheme 11.



Scheme 12.



Scheme 13.

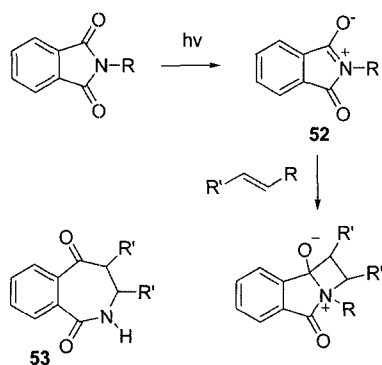


Scheme 14.

irradiation in an MeCN solution containing acrylonitrile (Scheme 12) exemplifies the operation of the latter ylide-forming photofragmentation pathway.

A priori, the excited states of *N*-phthaloyl derivatives of β -hydroxy- α -amino acids **44** can react by either of the two azomethine ylide-forming routes described above. Photodecarboxylation of these substrates would yield, β -hydroxy ylides **45**, while retro-aldol-like cleavage would form carboxy ylides **46** (Scheme 13). To evaluate the relative efficiencies of these two potentially competitive processes and to determine the chemical properties of the unusually substituted ylides generated by these routes, we investigated the photochemistry of *N*-phthaloyl derivatives of serine **47** and threonine **48** [27]. Irradiation of MeCN solutions of **47** and **48** gives rise, in each case, to a mixture of products in which the respective *N*-vinylphthalimides **49** and **50** predominate (Scheme 14). The presence of 65 mM methyl acrylate has little effect on the nature of these photoreactions. Accordingly, irradiation of MeCN solutions of **47** and **48**, each containing methyl acrylate, results in predominant formation of the vinylphthalimides **49** and **50** along with only minor amounts of the benzopyrrolizidine adduct **51**.

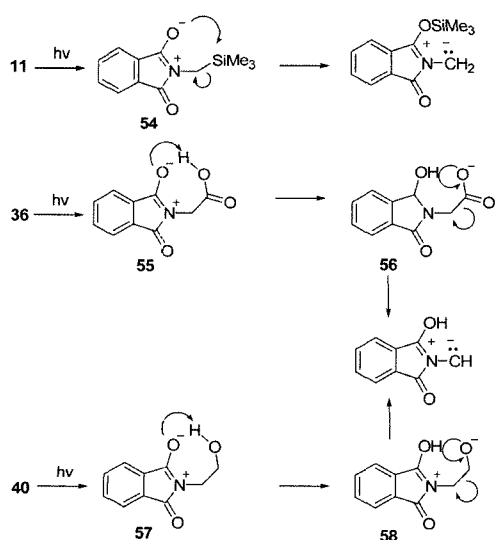
Two important conclusions can be drawn from the results of these studies. First, photodecarboxylation is the major reaction pathway followed by excited states of *N*-phthaloyl- α -amino- β -hydroxy acids. Second, hydroxyazomethine ylides, formed in the photochemistry of these substrates, are exceptionally short-lived, not readily trapped intermediates. This is a consequence of the existence of a facile elimination



Scheme 15.

route which efficiently transforms these ylides into *N*-vinylphthalimides.

It is instructive to question whether the azomethine ylide-forming photoreactions of *N*-(silylmethyl)phthalimides and those of the *N*-phthaloyl- α -amino acids and α -aminoalcohols share common mechanistic features. Above, we discussed these processes in terms of both SET-silyl-transfer and hydrogen abstraction mechanisms. However, from a unified perspective the reactions can be viewed as originating from a common polarized phthalimide excited state. Dipolar structures **52** have been invoked to explain photocycloaddition reactions of phthalimides with non-electron-rich alkenes (Scheme 15) [15, 16, 31]. Addition of an alkene to **52** is believed to be the key mechanistic step in these processes, which lead to formation of benzazepinedione products **53**. By using the dipolar description of phthalimide excited states, it is possible to develop an alternate and perhaps more encompassing picture of the ylide-forming photoreactions. For example, the conversion of (silylmethyl)phthalimide excited states **54** to the corresponding ylide can be viewed as



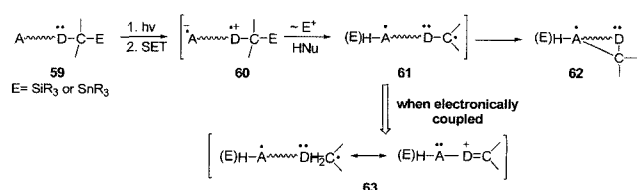
Scheme 16.

a 1,4-sigmatropic rearrangement or an internal nucleophilic substitution at silicon (Scheme 16). Similarly, rearrangement of acid- and alcohol-derived dipolar excited states **55** and **57** by proton transfer would set the stage for polar fragmentation of the resulting zwitterions **56** and **58** to form ylides. Independent of which mechanistic description is employed to explain the ylide-forming photoreactions, it is clear that the process can serve as the foundation for novel methods to prepare interestingly structured and functionalized *N*-heterocyclic products.

SET-Promoted 1,4-Dipole Forming Photoreactions of α -Ketoamides

More recent efforts in our laboratories led to the discovery, mechanistic delineation and synthetic application of a variety of other photochemical processes that are promoted by excited state SET. We have investigated photoreactions of linked donor-acceptor substrates **59** (Scheme 17) [32-38], which take place through the intermediacy of zwitterionic biradicals **60**. Because these intermediates contain radical cation sites with SiR_3 or SnR_3 α -electrofugal groups, they undergo rapid heterolytic fragmentation reactions ($\text{E}^+ = \sim\text{R}_3\text{Si}^+$ or $\sim\text{R}_3\text{Sn}^+$) that form biradicals **61**. These processes generate biradicals that then undergo C-C bond formation to form cyclic products **62**. The investigations have shown that photochemical reactions following this general pathway can be used to produce a wide variety of functionally and structurally complex targets, including macrocyclic polyethers [36, 37], polythioethers [37], polyamides [35, 37], and polypeptides [38]. In addition, these processes have served as the platform for a broad investigation aimed at gaining fundamentally important information about the factors that govern the chemical and quantum efficiencies of SET promoted photochemical reactions of polydonor linked acceptor systems [40].

As discussed above, an interesting subgroup of excited state reactions that follow the sequential SET-heterolytic fragmentation route are those which generate dipolar azomethine ylide intermediates. As depicted in Scheme 17, this occurs when electronic coupling (conjugation) between the radical centers in the ultimate biradicals **63** is possible. This behavior is seen in the photochemistry of *N*-trimethylsilylmethyl-phthalimides [25, 26], *N*-trimethylsilylmethyl-maleimides [27], *N*-trimethylsilylmethyl-arylimides [27], *N*-phthaloyl- α -amino acids and *N*-

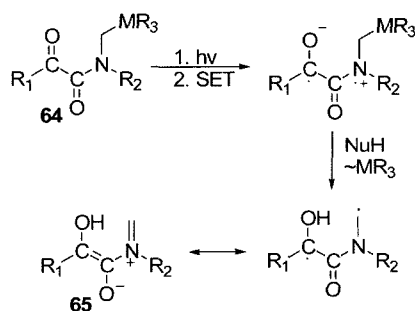


Scheme 17.

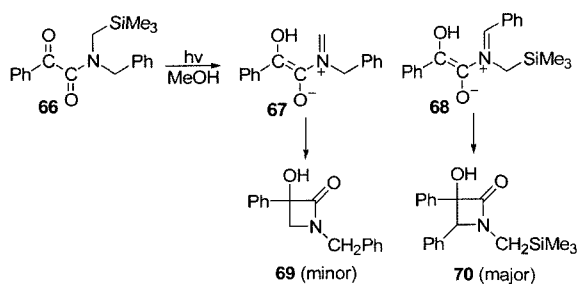
phthaloyl- β -amino alcohols [28]. Irradiation of these substrates results in formation of azomethine ylides (1,3-dipoles).

Based on the observations made in this effort, we postulated that irradiation of α -trialkylsilyl- and α -trialkylstannyl substituted α -ketoamides of general structure **64** (Scheme 18) would promote sequential SET-trialkylmetal (R_3Si or R_3Sn) migration to produce 1,4-dipoles **65**. Initial studies probing this issue [41] demonstrated that excited states of the silicon-substituted substrates follow this reaction pathway to form 1,4-dipoles, but only inefficiently. For example, β -lactam **69** is formed upon irradiation of the silyl-ketoamide **66** in MeOH (Scheme 19) through a sequential SET-trimethylsilyl transfer route, which generates 1,4-dipole **67**. However, this process ineffectively competes with more efficient excited state H-atom transfer induced formation (*via* dipole **68**) of the silicon containing β -lactam **70**.

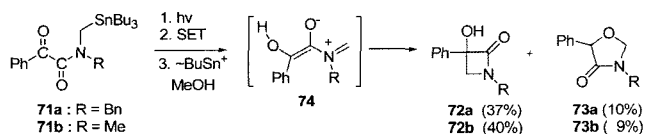
As predicted based on oxidation potential [42-44] and bond dissociation energy considerations, excited states of the corresponding α -tributylstannyl-substituted α -ketoamides react more selectively and efficiently by the sequential SET-trialkylmetal group transfer pathway. This is exemplified by the efficient transformation of the ketoamides **71a-b** to β -lactams **72a-b** and oxazolidinones **73a-b** upon irradiation in MeOH (Scheme 20).



Scheme 18.



Scheme 19.



Scheme 20.

This study showed that N-ributylstannylmethyl substituted α -ketoamides **71a-b** serve as precursors of 1,4-dipolar intermediates **74**, generated by a photoinduced SET-stannyl transfer pathway (Scheme 21). Once formed, the dipoles undergo facile electrocyclization or polar cyclization reactions to produce β -lactams and oxazolidinones, respectively. The absence of dipole forming photoreactivity of related trimethylsilyl-substituted ketoamides highlights a critical requirement of this method for 1,4-dipole generation. Specifically, successful operation of this process requires proper matching of the redox potentials of the excited state electron acceptor (imide *vs.* α -ketoamide) and the ground state donor (α -silylimide *vs.* α -stannylamide) in order to insure high rates for the key SET-step which competes with other excited state reaction pathways (*e.g.* H-atom abstraction).

An advantageous feature of this method for 1,4-dipole formation lies in its highly regioselective nature. Thus, unlike α -ketoamide H-atom abstraction processes, studied earlier by Aoyama and others [45-49], the SET-stannyl transfer route results in 1,4-dipole (Scheme 20) formation exclusively at the α -carbon that possesses an $SnBu_3$ group.

ACKNOWLEDGEMENTS

The authors are indebted to their enthusiastic and productive coworkers who contributed to the investigations described in this review. Financial support for the studies serving as the focus of this review was provided by grants from the Korea Research Foundation (MOEHRD, Basic Research Promotion Fund, R05-2004-000-10557-0) (to U.C.Y.) and the National Science Foundation (to P.S.M.).

REFERENCE

- Coyle, J. D. (1984) Phthalimide and its derivatives. In: *Synthetic Organic Photochemistry*. Ed. by Hospool, W. M. Plenum Press, NY pp.259-284.
- Mazzocchi, P. H. (1981) The photochemistry of imides. In: *Organic Photochemistry*. Padwa, A., Ed. by Marcel Dekker, NY 5 pp. 421-471
- Kanaoka, Y., Yoshida, K. and Hatanaka, Y. (1979) Photoaddition of olefins to cyclic imides: intermolecular oxetane formation and ring expansion. *J. Org. Chem.* **44**, 664-666.
- Kanaoka, Y., (1978) Photoreactions of cyclic imides. Examples of synthetic organic photochemistry. *Acc. Chem. Res.* **11**, 407-413.
- Kanaoka, Y., Koyama, K., Flippen, J. L., Isabella L. Karle and Witkop, B. (1974) Photochemistry of the phthalimide system. VI. Photocyclization of N-alicyclic phthalimides. Synthesis of multicyclic benzazepine systems. *J. Am. Chem. Soc.* **96**, 4719-4721.
- Coyle, J.D., Harriman, A. and Newport, G (1979) Reversible photorearrangement of N-substituted phthalimides: a flash photolysis study. *J. Chem. Soc., Perkin 2:Phys. Org. Chem.* **6**, 799-802.

7. P. Wagner. and B. S. Park. (1991) Photoinduced Hydrogen Atom Abstraction by Carbonyl Compounds In: *Organic Photochemistry*. Ed. by A. Padwa., **11**, pp. 227-366
8. Nakai, H., Sato, Y., Ogiwara, H., Mizoguchi, T. and Kanaoka, Y. (1974) Photoinduced reactions. XX. Photochemistry of the phthalimide system. IX. Photochemical synthesis of an oxazolo[4,3- α]isoindole-1-spiro ring system. *Heterocycles*. **2**, 621-624.
9. Sato, Y., Nakai, H., Wada, M., Ogiwara, H., Mizoguchi, T., Migita, Y., Hatanaka, Y. and Kanaoka, Y. (1982) Photochemistry of the phthalimide system. 23. Photocyclization of N-alkoxyalkylphthalimides with favored d-hydrogen abstraction: Syntheses of oxazolo[4,3- α]isoindoles and oxazolo[4,3- α]isoindole-1-spiro-1'-cycloalkane ring systems. *Chem. Pharm. Bull.* **30**, 1639-1645.
10. Sato, Y., Nakai, H., Ogiwara, H. and Migita, T. M. and Kanaoka, Y. (1973) Photochemistry of the phthalimide system. V photocyclization of the phthalimides with a sulfide chain: synthesis of aza-cyclols by δ , ϵ and ζ hydrogen abstraction. *Tetrahedron Lett.* **14**, 4565-4568
11. Kanaoka, Y., Nagasawa, C., Nakai, H., Sato, Y., Ogiwara, H., Mizoguchi, T. (1975) Photochemistry of the phthalimide system. XI. Photoinduced reactions. XXII. Photochemical synthesis of indolo[2,1- α]isoindole derivatives by the cyclization of N-(o-tolyl)phthalimides. *Heterocycles*. **3**, 553-556.
12. Yoon, U. C., Kim, H. J. and Mariano, P. S. (1989) Electron Transfer-Induced Photochemical Reactions in Imide-RXCH₂TMS Systems. Photoaddition of -Trimethylsilyl Substituted Heteroatom Containing Compounds to Phthalimides. *Heterocycles*. **29**, 1041-1064
13. Yoon, U. C., Cho, S. J., Oh, J. H., Lee, J. G., Kang, K. T. and Mariano, P. S. (1991) Photocyclization reactions of phthalimide- α -silyl-n-electron donor systems via singlet single electron transfer and triplet hydrogen abstraction and silyl group abstraction pathways. *Bull. Korean Chem. Soc.* **12**, 241-243.
14. Yoon, U. C., Oh, J. H., Lee, S. J., Kim, D. U., Lee, J. G., Kang, K. T., Mariano, P. S. (1992) Photocyclization reactions of N-[[trimethylsilyl]methoxy]alkyl] phthalimides. Efficient and regioselective route to heterocycles. *Bull. Korean Chem Soc.*, **13**, 166-172.
15. Maruyama, K., Kubo, Y. (1978) Photo-induced solvent-incorporated addition of N-methylphthalimide to olefins. Reactions promoted by way of initial one electron transfer. *Chem. Lett.*, **8**, 851-854.
16. Mazzocchi, P. H., Minamikawa, S. and Wilson, P. I. (1979) Photochemical addition of alkenes to N-methylphthalimide. Stereochemistry of the addition. *J. Org. Chem.* **44**, 1186-1188.
17. Kyushin, S., Masuda, Y., Matsushita, K., Nakadaira, Y. and Ohashi, M. (1990) Novel alkylation of aromatic nitriles via photo-induced electron transfer of group 14 metal-carbon σ donor. *Tetrahedron Lett.* **31**, 6395-6398
18. Lee, Y. J., Ling, R., Mariano, P. S., Yoon, U. C., Kim, D. U. and Oh, S. W. (1996) Exploratory Studies of H-Atom Abstraction and Silyl-Transfer Photoreactions of Silylalkyl Ketones and (Silylalkyl)phthalimides. *J. Org. Chem.* **61**, 3304-3314.
19. Yoon, U. C., Oh, S. W., Lee, S. M., Cho, S. J., Gamlin, J. and Mariano, P. S. (1999) A Solvent Effect that Influences the Preparative Utility of N-(Silylalkyl) Phthalimide and N-(Silylalkyl) Maleimide Photochemistry. *J. Org. Chem.* **64**, 4411-4418.
20. Ingold, K. U., Roberts, B. P. (1971) In: *Free Radical Substitution Reactions*. Ed. by Wiley, NY
21. Razuvaev, G. A., Vasileiskaja, N. S. and Muslin D. V. (1967) Rearrangement of 2,4-di-tert-butyl-6-trimethylsilylphenoxy. *J. Organomet. Chem.*, **7**, 365-533
22. Brook, A. G. and Duff, J. M. (1967) The Photochemistry of Silyl Ketones in Alcohol. *J. Am. Chem. Soc.* **89**, 454-455.
23. Alberti, A., Dellonte, S., Paradisi, C., Roffia, S. and Pedulli, G. F. (1990) Reactions of triplet carbonyl compounds and nitro derivatives with silanes. *J. Am. Chem. Soc.* **112**, 1123-1129.
24. Sato, Y., Nakai, H., Mizoguchi, T., Kawanishi, M., Hatanaka, Y. and Kanaoka, Y. (1982) Photochemistry of the Phthalimide System 20. Photodecarboxylation of N-Phthaloyl- α -Amino Acids. *Chem. Pharm. Bul.* **30**, 1263-1270.
25. Yoon, U. C., Kim, D. U., Kim, J. C., Lee, J. G., Mariano, P. S., Lee, Y. J. and Ammon, H. L. (1993) The Operation of H-Atom and TMS-Group Transfer Processes in the Photochemistry of Silylamidoalkyl-Ketones and Silylalkyl-Ketones and Silylalkyl-Phthalimides. *Tetrahedron Lett.* **34**, 5855-5858.
26. Yoon, U. C., Kim, D. U., Lee, C. W., Choi, Y. S., Lee, Y.-J., Ammon, H. L. and Mariano, P. S. (1995) Novel and Efficient Azomethine Ylide Forming Photoreactions of N-(Silylmethyl) phthalimides and Related Acid and Alcohol Derivatives. *J. Am. Chem. Soc.* **117**, 2698-2710.
27. Yoon, U. C., Cho, S. J., Lee, Y. J., Mancheno, M. J. and Mariano, P. S. (1995) Investigation of Novel Azomethine Ylide-Forming Photoreactions of N-Silylmethylimides. *J. Org. Chem.* **60**, 2353.
28. Yoon, U. C., Lee, C. W., Oh, S. W. and Mariano, P. S. (1999) Exploratory Studies Probing the Intermediacy of Azomethine Ylides in the Photochemistry of N-Phthaloyl Derivatives of α -Amino Acids and β -Amino Alcohols. *Tetrahedron*. **55**, 11997-12008.
29. Takahashi, Y., Miyashi, T., Yoon, U. C., Oh, S. W., Mancheno, M., Su, Z., Falvey, D. F. and Mariano, P. S. (1999) Mechanistic Studies of the Azomethine Ylide-Forming Photoreactions of N-(Silylmethyl)-phthalimides and N-Phthaloylglycine. *J. Am. Chem. Soc.* **121**, 3926-3932.
30. Huisgen, R., Scheer, W., and Huber, H. (1967) Stereospecific Conversion of cis-trans Isomeric Aziridines to Open-Chain Azomethine Ylides. *J. Am. Chem. Soc.* **89**, 1753-1755.
31. Maruyama, K., Kubo, Y. (1981) Photochemistry of N-(2-Alkenyl)phthalimides. Photo-induced Cyclization and Elimination Reactions. *J. Org. Chem.* **46**, 3612-3622.
32. Yoon, U. C. Oh, J. H. Lee, S. J. Kim, D. U. Lee, J. G. Kang, K.T. and Mariano, P. S. (1992) Photocyclization Reactions of N-(Trimethylsilylmethoxyalkyl)Phthalimides. *Bull. Korean Chem. Soc.* **13**, 166-1772
33. Yoon, U.C., Lee, S.J., Lee, K.J., Cho, S.J., Lee, C.W. and Mariano, P.S.. (1994) Exploratory Study of Photocyclization Reactions of N-(Trimethylsilylmethylthioalkyl)phthalimides.

- Bull. Korean Chem. Soc.*, **15**, 154-161.
34. Yoon, U.C., Cho, S.J., Oh, J.H., Kang, K-T., Lee, J.G. and Mariano, P.S. (1991) Photocyclization Reactions of Phthalimide- α -Silyl-n-Electron Donor Systems via Singlet Single Electron Transfer and Triplet Hydrogen Abstraction and Silyl Group Abstraction Pathways. *Bull. Korean Chem. Soc.* **12**, 241-243.
 35. Yoon, U.C., Kim, J.W., Ryu, J.Y., Cho, S.J. Oh, S.W. and P.S. Mariano. (1997) Single electron transfer-induced photocyclization reactions of N-[(N-trimethylsilylmethyl)aminoalkyl] phthalimides. *J. Photochem. Photobiol.* **106**, 145-154
 36. Yoon, U. C., Oh, S. W. and Lee, C. W. (1995) Efficient and regioselective photocyclization reactions of N-[(α -trimethylsilylmethoxy)polyoxalkyl]phthalimides to azacrown ethers. *Heterocycles*. **41**, 2665-2682.
 37. Yoon, U. C., Oh, S. W., Lee, J. H., Park, J. H., Kang, K. T. and Mariano, P. S. (2001) Applications of Phthalimide Photochemistry to Macrocyclic Polyether, Polythioether, and Polyamide Synthesis. *J. Org. Chem.* **66**, 939-943.
 38. Aoyama, H., Hasegawa, T., Watabe, M., Shiraishi, H. and Omote, Y. (1978) Photochemical reactions of N,N-disubstituted α -oxoamides. *J. Org. Chem.* **43**, 419-422,
 39. Yoon, U.C., Jin, Y.X., Oh, S.W., Cho, D.W., Park, K.H. and Mariano, P.S. (2002) Comparison of Photomacrocyclization Reactions of Trimethylsilyl- and Tributylstannyl-Terminated phthalimido- and Maleimido-Polyethers, *J. Photochem. Photobiol. A: Chem.* **150**, 77-84.
 40. Yoon, U.C., Kwon, H.C., Hyung, T.K., Choi, K.H., Oh, S.W., Yang, S., Zaho, Z. and Mariano, P.S. (2004) The Photochemistry of Polydonor-Substituted {phthalimides: Curtin-Hammett-Type Control of Competing Reactions of Potentially Interconverting Zwitterionic Biradical Intermediates, *J. Am. Chem. Soc.* **126**, 1110-1124.
 41. Wang, R., Chen, C., Duesler, E., Mariano, P.S. and Yoon, U.C. (2004) Photochemical Reactions of N-Trimethylsilylmethyl and N-Tributylstannylmethyl Substituted α -Ketoamides, *J. Org. Chem.* **69**, 1215-1220
 42. Yoshida, J., Itoh, M. and Isoe, S. (1993) Electrooxidative coupling of α -heteroatom-substituted organostannanes and organo silanes. *J. Chem. Soc., Chem. Commun.* **6**, 547-549
 43. Yoshida, J. I., Takada, K., Ishichi, Y. and Isoe, S. (1994) Anodic cyclization of unsaturated α -stannyl ethers. Termination by bromide derived from dibromomethane *J. Chem. Soc., Chem. Commun.* **20**, 2361-2362
 44. Yoshida, J., Ishichi, Y. and Isoe, S. (1992) Intramolecular carbon-carbon bond formation by the anodic oxidation of unsaturated alpha-stannyl heteroatom compounds. Synthesis of fluorine containing heterocyclic compounds. *J. Am. Chem. Soc.* **114**, 7594-7595.
 45. Hasegawa, T., Watabe, M., Aoyama, H. and Omote, Y. (1977) The photochemical reactions of N,N-dialkyl α,β -unsaturated amides. *Tetrahedron*. **33**, 485-488.
 46. Aoyama, H., Hasegawa, T., Watabe, M., Shiraishi, H. and Omote, Y (1978) Photochemical reactions of N,N-disubstituted alpha-oxoamides. *J. Org. Chem.* **43**, 419-422.
 47. Aoyama, H., Sakamoto, M. and Omote, Y. (1881) Photochemical reactions of N-alkyl- α -oxoamides. *J. Chem. Soc., Perkin Trans.* **1**, 1357-1359
 48. Aoyama, H., Sakamoto, M., Kuwabara, K., Yoshida, K. and Omote, Y. (1983) Photochemical reactions of alpha-oxoamides. Norrish type II reactions via zwitterionic intermediates. *J. Am. Chem. Soc.* **105**, 1958-1964.
 49. Chesta, C. A. and Whitten, D. G. (1992) Photocyclization of alpha-ketoamides amides in homogeneous solution and aqueous cyclodextrin media. The role of zwitterions and diradicals in photoinduced electron transfer reactions. *J. Am. Chem. Soc.* **114**, 2188-2197.