

A Novel Azomethine Ylid Forming Photoreaction of N-Trimethylsilylmethylphthalimides

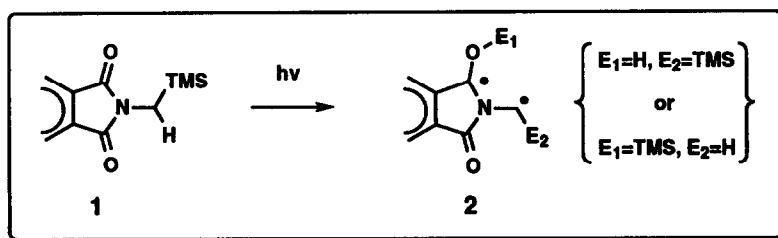
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Abstract. Irradiation of N-trimethylsilylmethylphthalimide and its 1,8-naphthalimide analog leads to generation of azomethine ylids by C to O TMS-transfer processes.

Recent studies¹ probing the excited state chemistry of N-silylalkylphthalimides and arylketones have provided us with an opportunity to investigate the photochemistry of N-CH₂TMS-substituted phthalimides of general structure **1**. This effort has led to the discovery of an interesting photochemical process involving C to O TMS-migration to produce azomethine ylids. Observations revealing this novel excited state reactivity are described below.

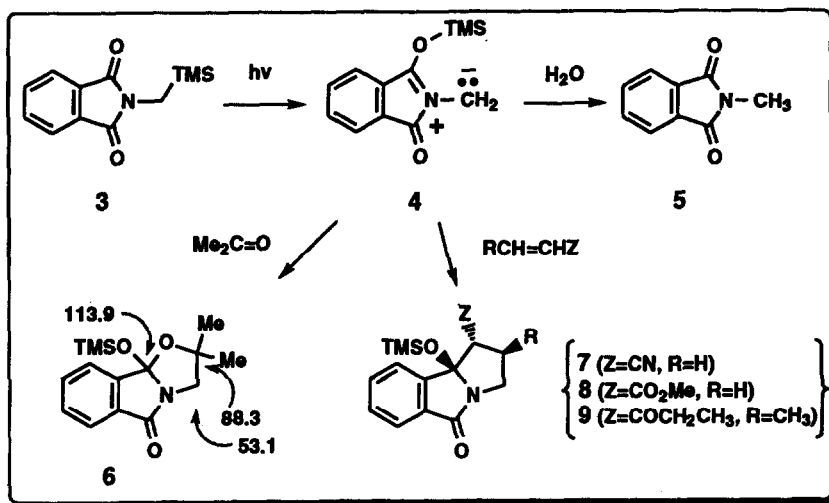
At the outset, our expectations about the photochemistry of these substances were biased by the results of parallel studies which showed that silylalkylphthalimides, analogous aryl silylalkyl ketones and silylmethylamido ketones undergo both H-atom abstraction and TMS-transfer reactions upon irradiation.^{1b} Thus, among the reaction pathways that could be available to the excited states of **1** were those leading to formation of diradical (if triplet) / ylid (if singlet) intermediates related to **2**.



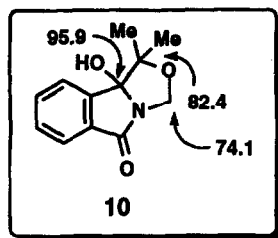
Initial studies of the photochemistry of the N-trimethylsilylmethylphthalimide **3** provided deceptively simple results. Accordingly, irradiation (Pyrex) of an MeCN solution of **3** leads to efficient production (83%) of the N-Me analog **5** (Scheme 1). Our interest in this process was heightened by the observation that photoreaction of **3** in D₂O-CH₃CN (and not H₂O-CD₃CN)

gives the N-CDH₂ analog of **5**. The implication here is that the hydrogen in **5** derives by protonation of an anionic carbon center rather than by radical H-atom abstraction.

Scheme 1.



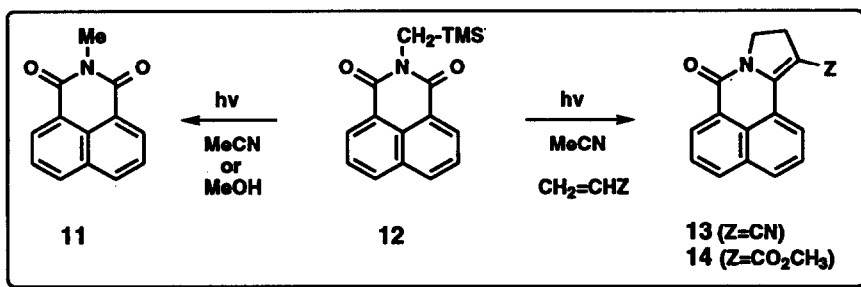
Information about the process occurring came from the observed formation of O-TMS containing adduct **6** (67%) from photoreaction of **3** in $Me_2C=O$. The regiochemical assignment in **6** is based on comparative ¹H- and ¹³C-NMR data for **6** and an analog of its isomer **10**, prepared earlier by Kanaoka² (see structures for representative ¹³C-NMR shifts) and on the transformation of **6** to the N-CH₂C(Me)₂OH phthalimide by treatment with aq. HCl.



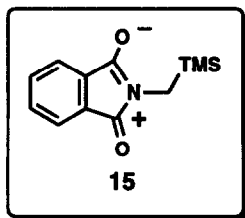
The above result suggest that irradiation of **3** lead to novel formation of the ylid **4** (either directly from 3^{S1} or following diradical ISC from 3^{T1}) which undergoes C-protonation and imidate desilylation to furnish **5** or dipolar cycloaddition to $Me_2C=O$ giving adduct **6**. Additional observations that confirm the ylid forming C to O TMS migration nature of the process and that reveal stereochemical details have come from the results of trapping reactions. Irradiation of **3** in MeCN containing 85 mM $CH_2=CHCN$ or $CH_2=CHCO_2Me$ results in efficient production of the respective adducts **7** (81%) and **8** (93%), both as single diastereomers. The endo-CN

stereochemistry of **7** is revealed by x-ray crystallographic analysis and that of **8** follows from comparisons of its NMR properties with those of **7**. Thus, it appears that dipolar cycloaddition of **4** with EWG-substituted olefins are both highly regioselective and stereoselective. The potential stereospecific nature of the trapping reactions is evidenced by the fact that the *trans, trans*-adduct **9** (by x-ray analysis) is formed exclusively upon irradiation of **3** in the presence of *trans*-hex-4-en-3-one. Finally, irradiation of **3** in MeC=O solutions containing CH₂=CH-CO₂Me gives only the acrylate trapping product **8** even when acrylate concentrations are as low as 10 mM (at [CH₂-CHCO₂Me]=1 mM the 6:8 ratio is 6:1).³

The excited state of N-trimethylsilylmethyl-1,8-naphthalimide (**12**) participates in a related ylid forming C to O TMS migration process. For example, irradiation of **12** in either MeCN or MeOH gives the N-Me analog **11** (75%) while the cycloadducts **13** or **14** (ca. 18%) along with **11** (ca. 50%) are produced when MeCN solutions of **12** containing 70 mM CH₂=CHCN or CH₂=CHCO₂Me are irradiated. Two features of this chemistry are worthy of comment. Firstly, dipolar-trapping of the ylid formed from **12** is less efficient (vs. protonation) than for **4**. Secondly, cycloadducts formed in this way are more prone to β-elimination.



The ylid forming photoreactions of **3** and **12** are examples of TMS-abstractions by the carbonyl oxygen of phthalimide excited states. As such, the processes are TMS-analogs of the familiar⁴ Norrish Type II H-atom abstraction reactions of these and related imides. However, this process is unique to systems in which the TMS-group is linked to carbon adjacent to nitrogen since the related β- and γ-TMS compounds react by H-rather than TMS-migration exclusively when MeCN is used as solvent. This characteristic difference might lie in the fact phthalimide excited states possess larger internal CT-character⁵ reflected in the resonance representation **15**.



From this perspective, the migration process does not resemble classical, radical-like H-atom abstractions but rather is better viewed as a polar or sigmatropic group transfer. Finally, it should be noted that the N-Me analogs **5** and **11** do not undergo photoinduced C to O H-migrations to form ylids.⁶ However, Kanaoka demonstrated in an early study⁷ that N-phthalimide derivatives of α -amino acids react upon irradiation in $\text{Me}_2\text{C}=\text{O}$ to give decarboxylation products and, in one case, a trace amount of a cycloadduct. These observations suggest that ylids related to **4** (OH vs. OTMS) perhaps can be generated by an excited state proton transfer-decarboxylation relay also. Further studies are underway to probe the scope, mechanistic details and synthetic potential of the novel photochemical process described above.

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References.

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- (3) Qualitatively, the efficiency of disappearance of **3** for fixed time irradiations is reversely dependent on $[\text{CH}_2=\text{CHCO}_2\text{Me}]$ suggesting that this olefin quenches the excited state of **3** that serves as a precursor of **4**.
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- (6) The $\text{NCH}_2\text{CH}_2\text{TMS}$ -phthalimide does undergo, although inefficiently H-migration to the carbonyl oxygen from the N- CH_2 position (ref. 1a).
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