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Communications

Photocyclization Reactions of Phthalimide- α -Silyl- n -Electron Donor Systems via Singlet Single Electron Transfer and Triplet Hydrogen Abstraction and Silyl Group Abstraction Pathways

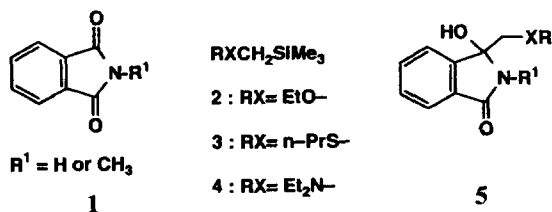
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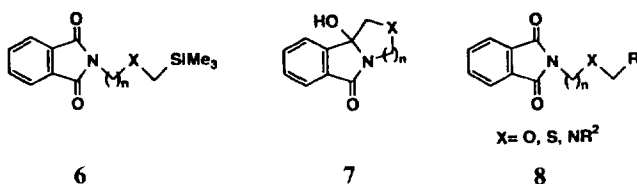
Our previous studies in the area of electron transfer (SET) photochemistry using α -silyl electron donors led to observations that (1) photoinduced SET-desilylation sequences serve as selective methods for carbon radical generation¹ and (2) SET-desilylation and SET-deprotonation pathways compete in photoaddition reactions between α -silylamine and cyclohexenones². The competition between these pathways are shown to be affected by reaction conditions which control the ratio between the formation of contact ion pair and that of solvent separated ion radical pair. In the study of photoinduced SET reaction of phthalimides, **1** with α -silyl- n -electron donors **2-4**³, we observed that photoaddition reactions occur to yield photoadducts **5** via SET-desilylation pathways, exclusively.



In a continuation of these efforts, we are investigating SET-induced photocyclization reactions of phthalimides which have α -silyl- n -electron donor groups appended **6**.

This work was guided by earlier observations⁴ of Kanaoka

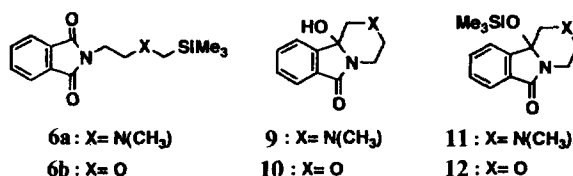
and Coyle made in photochemical reactions of N -substituted phthalimides via SET-deprotonation or hydrogen atom abstraction routes⁵. However the photocyclizations of compounds of several structures **8** studied by Kanaoka and Coyle suffered from low regioselectivity in the generation of intermediate carbon radicals and low product yields. Based on our previous studies of SET photochemistry using α -silyl- n -electron donors^{1,3}, we felt that photocyclizations of **6** could provide an efficient and regioselective methods for construction of heterocyclic compounds such as **7**.

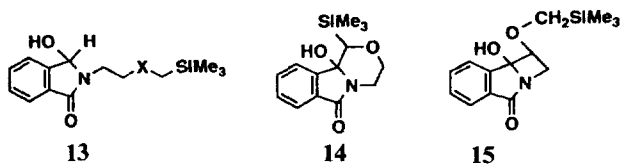


We now report preparative aspects of photocyclization reactions of **6** ($n=2$, $X=\text{N}(\text{CH}_3)$ and $X=\text{O}$) and new mechanistic observations in reactions involving singlet SET, triplet hydrogen atom abstraction and triplet silyl group abstraction processes.

Irradiation⁶ of phthalimide derivative **6a**⁷ in CH_3OH leads to production of cyclized products **9**(19%) and **11**(23%) along with reduced phthalimide ($X=\text{NCH}_3$) **13**(19%)⁷. The photoreaction of **6a** in a mixed solvent system, $\text{CH}_3\text{OH}/\text{acetone}$ (2 : 1) gives **9**(11%), **11**(34%) and **13**(34%) respectively with a faster rate than in CH_3OH .

Irradiation of **6b**⁷ in CH_3OH rapidly leads to high yielding production of the cyclized product **10**(98%) exclusively. Similarly to the case of **6a**, photoreaction of **6b** in acetone produces two additional cyclized products **12**(19%) and **14**(16%) along with the major cyclized product **10**(32%) with a slower rate. This is in contrast to the case of **6a** where the presence of acetone facilitates the photoreaction⁶.





Interestingly, noticeable changes occur in product distributions and reaction rates when acetone is used as solvent. These results suggest that phthalimide excited states responsible for formation of products, **11**, **12**, **13** and **14** are triplets in nature while those for cyclized products **9** and **10** are singlets. Support for these conclusions was gained from oxygen quenching experiments⁸. Oxygen does not affect the efficiency of formation of **10** and conversion rate in reaction of **6b** in CH₃OH while oxygen lead to partial quenching of the formation of **10** and complete quenching of the production **12** and **14** in acetone.

Similar results were obtained from oxygen quenching of photoreaction of **6a** in CH₃OH or CH₃OH/acetone(2/1) where the formation of **11** and **13** were completely quenched while the formation of **9** was not affected. Considering observations made in the present study and those made in the study of intermolecular photoinduced SET reactions of phthalimides **1** with α -silyl-n-electron donors **2-4** in CH₃OH or CH₃CN, it is likely that photoreaction of **6b** in methanol leading to exclusive formation of **10** follows an efficient singlet SET-desilylation pathway which overrides triplet reactions involving H-atom or SiMe₃ abstraction routes.

On the other hand photoreaction of **6b** in acetone and that of **6a** in CH₃OH or CH₃OH-acetone seem to proceed through triplet hydrogen abstraction (for formation of **13** and **14**) and triplet silyl group abstraction (for formation of **11** and **12**) pathways which compete with singlet SET processes (for formation of **9** and **10**). Silyl group abstraction¹⁰ by triplet carbonyl is predominant over hydrogen abstraction in these systems and is believed to be the first example of a reaction of this type to be reported. The formation of **14** by hydrogen abstraction¹¹ via eight-membered transition state instead of **15** via a typically more favorable six-membered transition state is indicative of a α -silyl group effect on weakening the C-H bond towards abstraction.

Considering the fact that tertiary amines have lower oxidation potentials³ and thus, are better electron donors than alkyl ethers, the photochemical behavior of **6a** seems strange in that (1) photoreaction of **6a** in CH₃OH is more sluggish than in acetone and (2) it gives predominantly triplet products **11**(23%) and **13**(19%) over the singlet SET product **9**(19%) even in CH₃OH.

In comparison **6b** gives only the singlet SET product **10**(98%) and undergoes faster conversion in CH₃OH. It is perhaps possible that the α -silylamine group acts as electron transfer quencher of the phthalimide singlet excited state¹². This intramolecular quenching can explain the sluggish reaction of **6a** in CH₃OH thus allowing the less efficient triplet reactions to compete.

We are continuing to explore the photocyclization reactions of phthalimides related to **6** with more methylene units between phthalimide and α -silyl electron donor sites in order to develop methods to construct larger heterocycles and to study mechanistic features such as triplet silyl group abstraction.

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References

- (a) M. A. Brumfield, S. L. Quillen, U. C. Yoon, and P. S. Mariano, *J. Am. Chem. Soc.*, **106**, 6855 (1984); (b) M. A. Brumfield, U. C. Yoon, E. Hasegawa, and P. S. Mariano, *J. Org. Chem.*, **53**, 5435 (1988).
- (a) U. C. Yoon, J. U. Kim, E. Hasegawa, and P. S. Mariano, *J. Am. Chem. Soc.*, **109**, 4421 (1987); (b) E. Hasegawa, W. Xu, P. S. Mariano, U. C. Yoon, and J. U. Kim, *J. Am. Chem. Soc.*, **110**, 8099 (1988).
- U. C. Yoon, H. J. Kim, and P. S. Mariano, *Heterocycles*, **29**, 1041 (1989).
- (a) Y. Kanaoka, *Acc. Chem. Res.*, **11**, 407 (1978); (b) J. D. Coyle, "Synthetic Organic Photochemistry" W. M. Horspool, ed., Plenum Press, New York, p. 259, 1984; (c) P. H. Mazzocchi, "Organic Photochemistry" A. Padwa, ed., Marcel Dekker, New York, Vol. 5, p. 421, 1981 and references therein.
- Kanaoka⁴ suggested that the reactions of phthalimides containing oxygen in the N-alkyl chain proceed via H atom abstraction and later suggested that those of phthalimides containing nitrogen or sulfur in the N-alkyl chain proceed through SET pathways when interest in SET induced photoreactions increased.
- Irradiation conditions are as following: Pyrex filter, N₂ atmosphere, 500 mg of **6a** or 1 g of **6b** in 200 ml of solvent, irradiation time, % conversion and solvent used, for **6a**; 7 h, 86%, CH₃OH; 3 h, 82%, CH₃OH/acetone(2/1), for **6b**; 2 h, ca. 100%, CH₃OH; 2 h, 60%, acetone. Reactions were monitored by tlc and product separations were by silica gel column chromatography and preparative tlc. The reported yields are for pure isolated substances.
- Synthetic and structure determination methods will be discussed in a full paper. The ¹H-NMR, ¹³C-NMR, IR, low and high resolution mass spectra of all new compounds were consistent with the assigned structures.
- Two solutions containing 50 mg of **6a** or **6b** in 20 ml of solvent were simultaneously irradiated in a Rayonet reactor with RUL-3000 lamps while a stream of N₂ and the other with a stream of O₂.
- Inefficient triplet SET is indicated to take place judging from partial quenching of **10** in the reaction of **6b** in CH₃OH.
- (a) This new reaction can be understood considering the characteristics of C-Si and C-H bonds (smaller bond dissociation energy of C-Si (318 kJ/mol) than that of C-H (420 kJ/mol) and greater bond energy of Si-O (531 kJ/mol) than O-H bonds (462 kJ/mol)^{10b}. (b) E. Colvin, "Silicon in Organic Synthesis" Butterworths, London, Chapter 2, 1981.
- (a) Hydrogen abstractions of other than γ -hydrogens have been observed^{11b-d} and abstraction by a triplet carbonyl of hydrogen α to silyl group and α to oxygen has also been observed in the photoreaction of acenaphthenequinone with α -silyl ether **2^{1e}**; (b) Y. Kanaoka, Y. Migita,

Y. Sato, and H. Nakai, *Tetrahedron Lett*, 51 (1973); (c) H. Nakai, Y. Sato, H. Ogiwara, T. Mizoguchi, and Y. Kanaoka, *Heterocycles*, 2, 621 (1974); (d) Y. Kanaoka and Y. Migita, *Tetrahedron Lett*, 3693 (1974); (e) U. C. Yoon, Y. C. Kim, J. J. Choi, and P. S. Mariano, manuscript in preparation.

12. (a) Mazzocchi observed that alkenes with lower ionization potential fail to photoadd to N-methylphthalimide and explained this by electron transfer quenching action (large k_{bet}) of alkenes with low oxidation potential^{12b}; (b) P. H. Mazzocchi, S. Minamikawa, and M. Bowen, *J. Org. Chem.*, 9., 1713 (1978).

Solid-State ¹³C-NMR Studies of Bis(oxalato)dioxovanadate(V) Complexes

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Vanadium(V) forms stable complexes with oxalate,¹⁻⁴ EDTA,^{5,6} and a few other ligands. The rarity of vanadium(V) complexes is due to its strong oxidizing power with most ligands being oxidized by the metal center.

Oxalate as a bidentate ligand has been of great interest in coordination chemistry for a long time.⁷ Oxalic acid is known to form irregular octahedral complexes with vanadium(V), and their structures having been assigned on the basis of X-ray diffraction studies^{1,2} are shown in Figure 1. In this paper we report the solid-state ¹³C-NMR spectra of (NH₄)₃[VO₂(C₂O₄)₂]·2H₂O and K₃[VO₂(C₂O₄)₂]·3H₂O and discuss them with relation to the structures. And ¹³C-NMR spectra of the complexes in solution are also discussed.

Solid (NH₄)₃[VO₂(C₂O₄)₂]·2H₂O and K₃[VO₂(C₂O₄)₂]·3H₂O

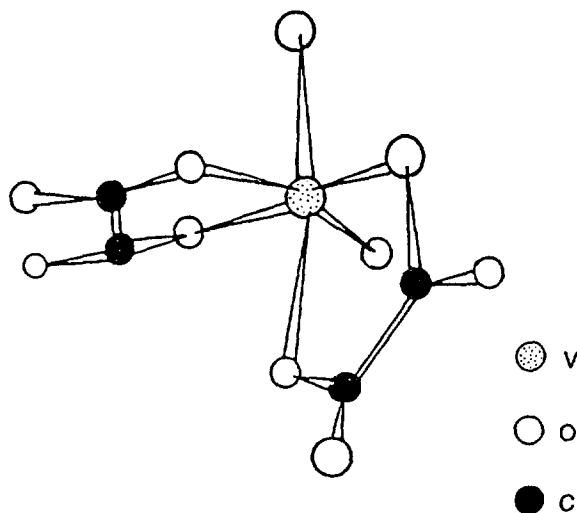


Figure 1. Irregular octahedral geometry of [VO₂(C₂O₄)₂]³⁻ ion.

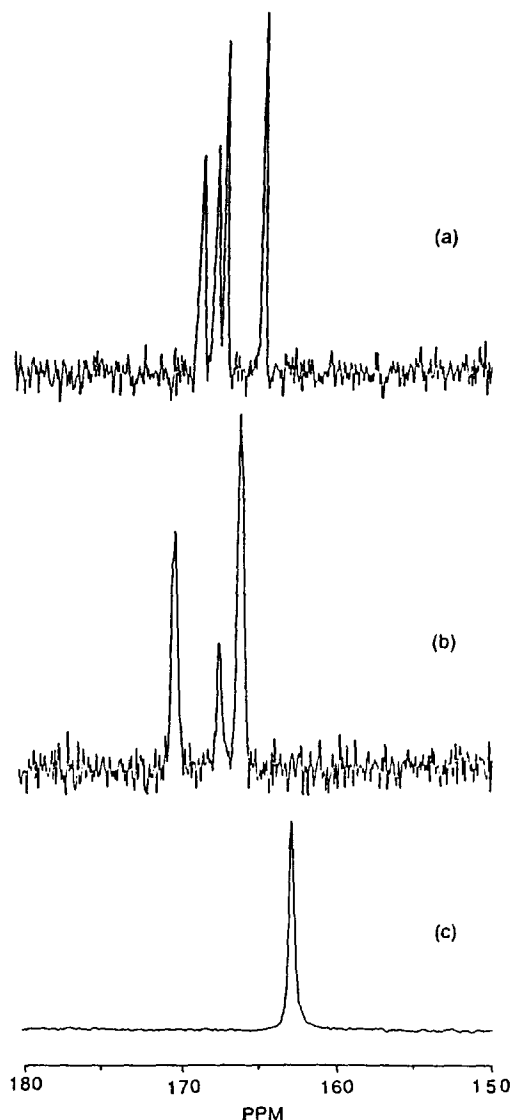


Figure 2. CP/MAS ¹³C-NMR spectra (75.47 MHz) of solid (a) (NH₄)₃[VO₂(C₂O₄)₂]·2H₂O, (b) K₃[VO₂(C₂O₄)₂]·3H₂O, and (c) H₂C₂O₄·2H₂O.

were prepared by the method of Sathyanarayana, *et al.*⁸ and by the method of Drew, *et al.*,² respectively.

¹³C NMR spectra of solid samples were recorded on a Bruker MSL-300 NMR spectrometer at 75.47 MHz with CP/MAS technique. A spectral width of 29411 Hz and an accumulation of ~200 transient with acquisition time of 0.85 s were used for obtaining ¹³C spectra of the solid samples. The contact time was 2 ms and the delay between each scan was 5 s. Chemical shifts were measured relative to the carboxylic carbon in glycine and reported according to the relation $\delta_{TMS} = \delta_{glycine} + 176.0$ ppm. ¹³C-NMR spectra of solution samples were recorded on a Bruker AM-250 NMR spectrometer at 62.90 MHz. ¹³C chemical shifts were measured relative to internal dioxane and reported according to the relation $\delta_{DSS} = \delta_{dioxane} + 69.14$ ppm.

According to the bond lengths in solid (NH₄)₃[VO₂(C₂O₄)₂]·2H₂O and K₃[VO₂(C₂O₄)₂]·3H₂O determined by X-ray diffraction studies^{1,2} two oxo oxygens in both complexes have short V=O bonds (1.628(2)-1.648(2) Å) which indicate strong