

## Novel Photocrosslinking Molecules

Kristi Simonton and Edward Fewkes  
Corning Inc. Organic Technology Group  
Sullivan Park R&D Center  
Painted Post, NY

### Introduction

UV cure free radical and cationic chemistry have enjoyed use in a wide variety of coating applications. Both of these systems have strengths which encourage their use in various applications, e.g., free radical photochemistry enjoys the benefit of speed and a large choice of available materials, while cationic systems are typically “living” polymerizations being capable of continuing reaction after the light source has been removed. In this paper we present some of our leading work to extend photocrosslinking reactions from the traditional cationic and free radical systems and investigate the use of photo-carbene molecules. We shall describe the differences between a carbene and other UV cure systems, discuss areas where carbenes are used and present results surrounding the use of these molecules in simple UV cure systems.

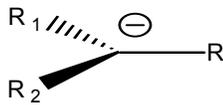
### Background

Carbenes are a class of reactive carbon centered molecules which are distinct from the other well known reactive intermediates - cations, anions and free radicals - as displayed in figure 1. A cationic molecule is typified by an absence of electrons leading to a net positive charge, while anionic molecules have an additional electron leading to a net negative charge. By contrast, both carbenes and free radicals are net neutral and contain orbitally unpaired electrons. A free radical contains one unpaired, non bonding electron, while a carbene consists of two non bonding, unpaired electrons.<sup>1</sup> An additional complication for a carbene molecule is the possibility for paired and unpaired spins on the electrons leading to molecules with either singlet or triplet spin characteristics. While the reactivity of a singlet or triplet carbene can be quite different, the issues surrounding this state will not be further addressed in this paper, but may be further understood by consulting the works described in reference 1.

(a) Carbocation



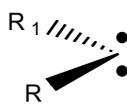
(b) Carboanion



(c) Free radical



(d) Carbene

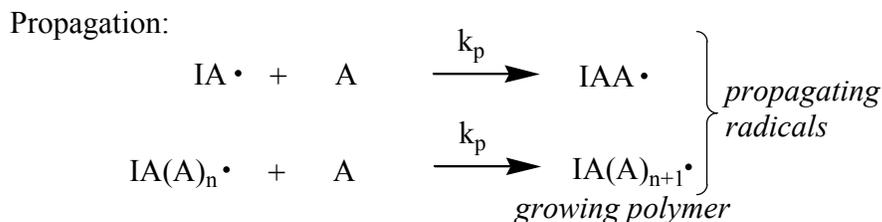
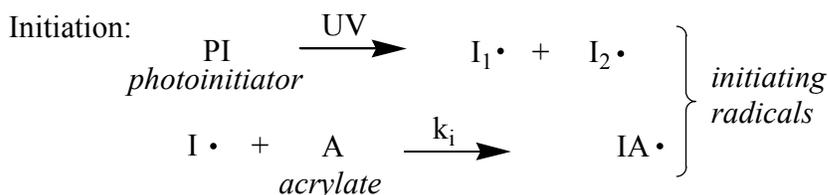


**Figure 1: Carbon centered reactive intermediates**

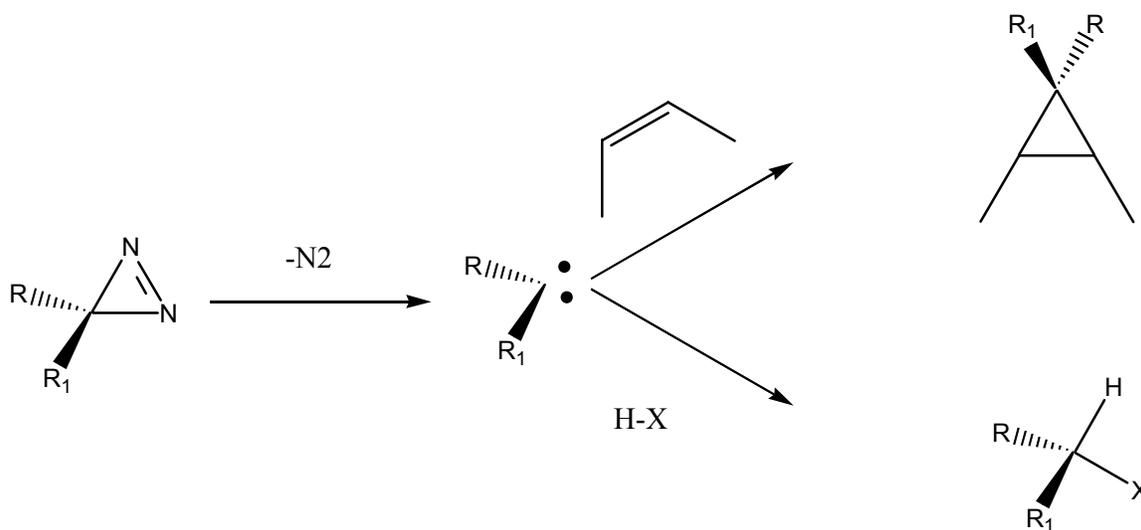
The reactivity of a carbene molecule differs from that of a free radical in several ways. As may be seen in figure 2 (a), a typical light initiated free radical cure reaction begins in the initiation step as the photoinitiator molecule forms two free radicals, which then may add across a double bond in a stepwise manner to lead to higher molecular weight molecules. By comparison, a photocarbene molecule does not require a separate initiator, but will reach its di-radical-like state directly after light absorption by expelling two bonds from a carbon atom center. The molecule typically expelled is nitrogen, and di-azo molecules are the typical starting materials for carbenes. A carbene, generally does not behave as a di-radical, but rather will insert either into a double bond or into a hydrogen containing single bond, as shown in figure 2

**Figure 2: Comparison of free radical and carbene reactions**

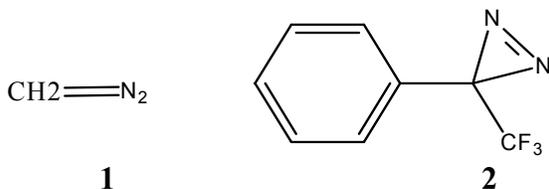
(a) Free Radical Acrylate Polymerization



(b) Carbene insertion

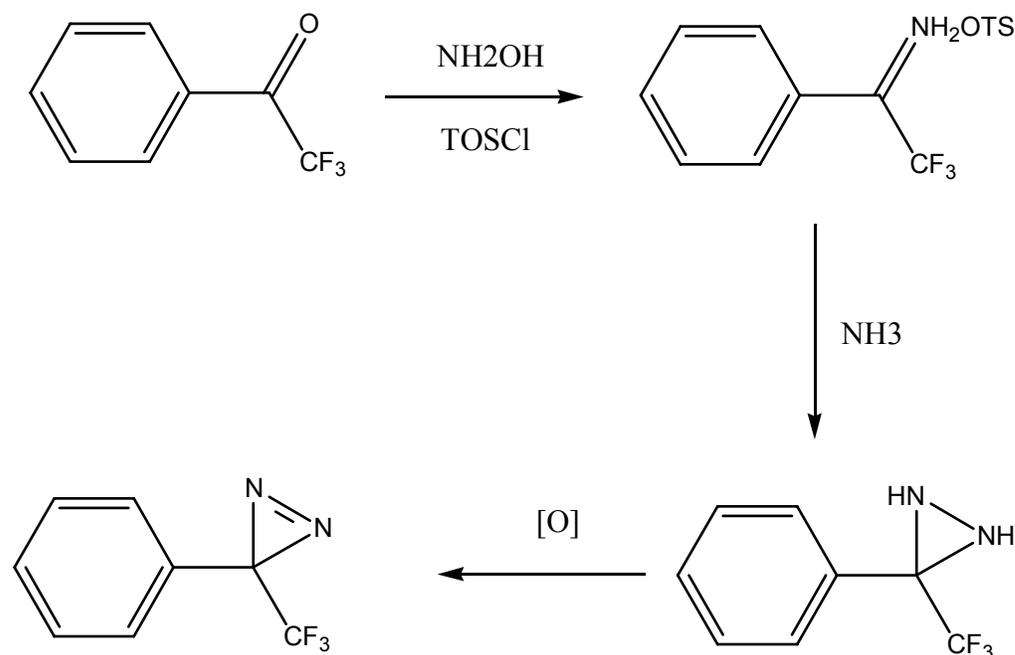


While industrial uses of metallocarbenes are well known for olefin polymerization, carbon centered carbenes have received much less attention outside of organic synthesis.<sup>2</sup> One reason for this is due to the few di-azo molecules available that are not extremely reactive. The classic example is the parent molecule di-azomethane (*1* in Figure 3), which is known to lose nitrogen explosively when exposed to ground glass joints and is therefore typically generated as needed, rather than synthesized and stored for later use. A notable exception to such highly reactive molecules, are those molecules based on 3-trifluoromethyl-3-phenyldiazirine (TFMPA, *2* in Figure 3).



**Figure 3: Carbene precursors**

Molecules containing the azirine functional group have been well documented as precursors for carbene formation.<sup>3</sup> TFMPA, in particular, is quite stable at room temperature, may be stored for extended periods of time (away from light), and as a result has seen a great deal of use in biological studies as a photo-affinity labeling agent.<sup>4, 5</sup> By way of demonstration of the ubiquitous use of molecules containing the TFMPA moiety, a sub-structure search conducted using SciFinder® software located 828 molecules containing this sub-structure.<sup>6</sup> Given the popularity of TFMPA in biology, it is no surprise that the synthesis of the molecule (scheme 1) must be reasonably straightforward and that some commercial sources of further functionalized molecules are also commercially available.<sup>7</sup> While highly reactive carbenes such as those from diazo methane will add across carbon-carbon double bonds or insert into carbon hydrogen bonds, the TFMPA carbene has been shown to insert best into N-H or O-H bonds.<sup>7</sup> Due to the similarity between the amide functionality found in polypeptides and that of the urethane functional group commonly used in UV cure urethane acrylate coatings, the possible use of this molecule as a novel cross linking agent seemed apparent.

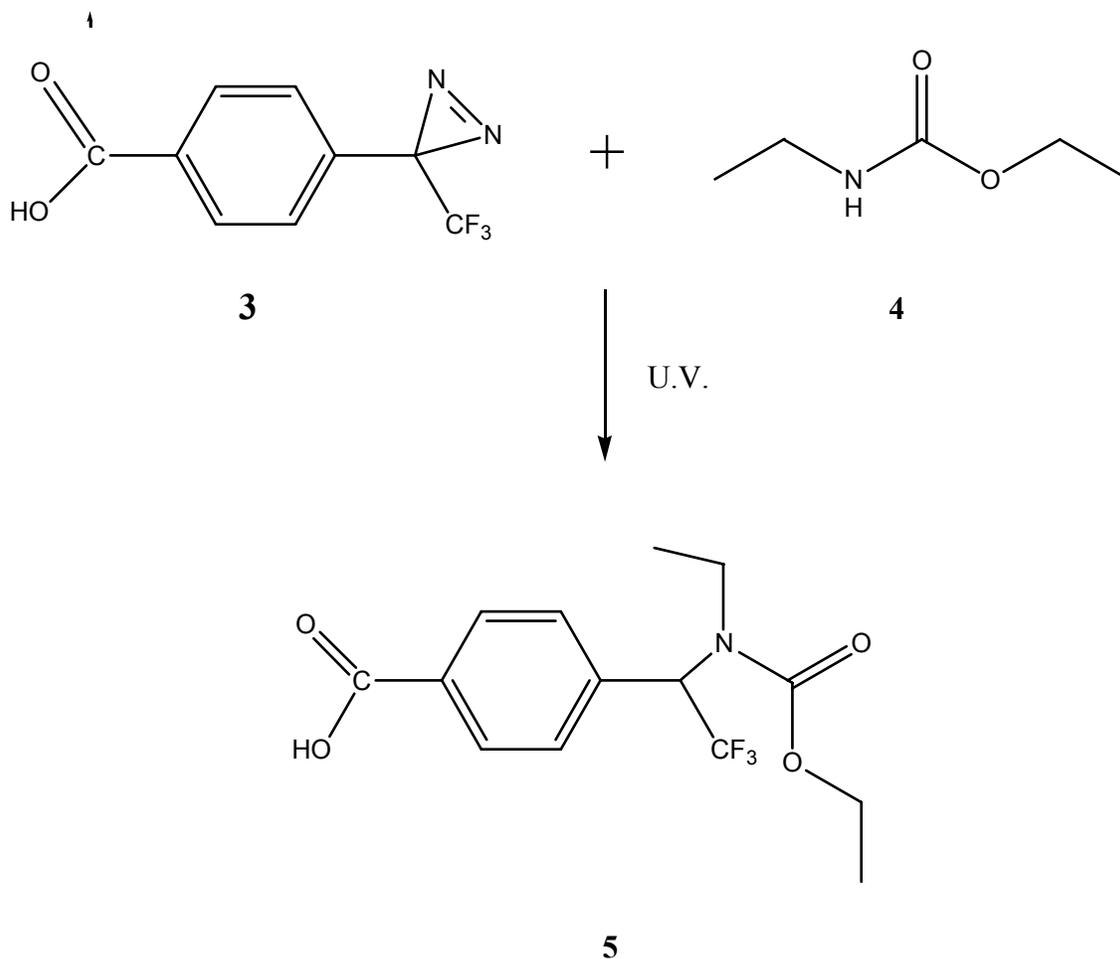


**Scheme 1: Synthesis of TFMPA**

## Results and Discussion

### *Model studies*

Our initial investigations into the reactivity of the TMFPA molecule began with determining the relative speed of reaction of this functional group with a urethane containing molecule. This was accomplished by following the course of the reaction shown in scheme 2 between molecule 3 (a commercially available TMFPA containing molecule) and N-ethylurethane 4 in a UV-Vis spectrophotometer. The use of 3 was advantageous for our study since it was not only a good model compound, but also a suitable candidate for synthesizing a crosslinker by virtue of the carboxylic acid group present in the para position of the aryl ring. The progress of the reaction was followed using the method described in reference 5 (c) and is shown in Figure 4. As may be seen, the loss of the azirine group absorption occurs steadily after light exposure and the growth of two new peaks after about 70 seconds becomes apparent. The complete characterization of the product of this reaction is on-going as of this writing to verify that the reaction product structure shown in scheme 2. Since both UV and chromatographic methods demonstrated the formation of a new product, not derived from carbene degradation, the decision was made to pursue the synthesis of a difunctional TMFPA containing molecule and to study its reaction with a commercially available urethane acrylate oligomer.



**Scheme 2: TFMPA model reaction**

*Synthesis of difunctional TMFPA carbene*

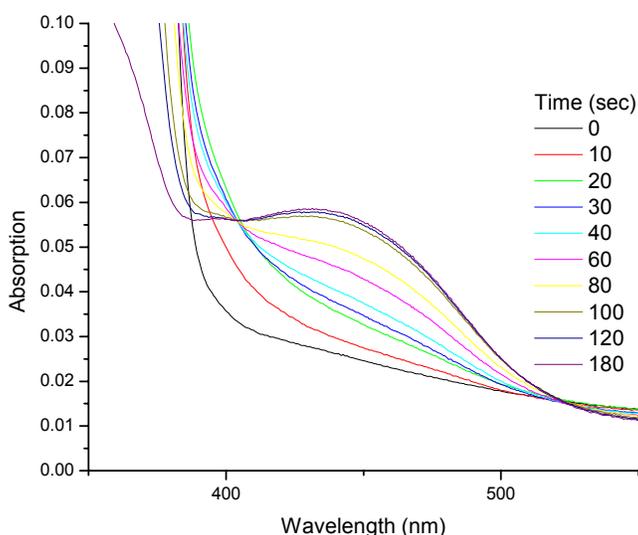
The synthesis of the difunctional molecule was accomplished by reacting 2.5 moles of 3 with di-iodopropane 6 in acetone/potassium carbonate as shown in Scheme 3 below. The reaction was straightforward, affording largely difunctional molecule 7, with a smaller amount of monofunctional 8 in X % (Add) total yield, as determined by GC/MS (see figure 5). (you need to add Figure 5) For purposes of this study, the mixture of 7 and 8 was used without further purification in reaction with [a] oligomer A.



### Scheme 3: Synthesis of di-azirine crosslinker

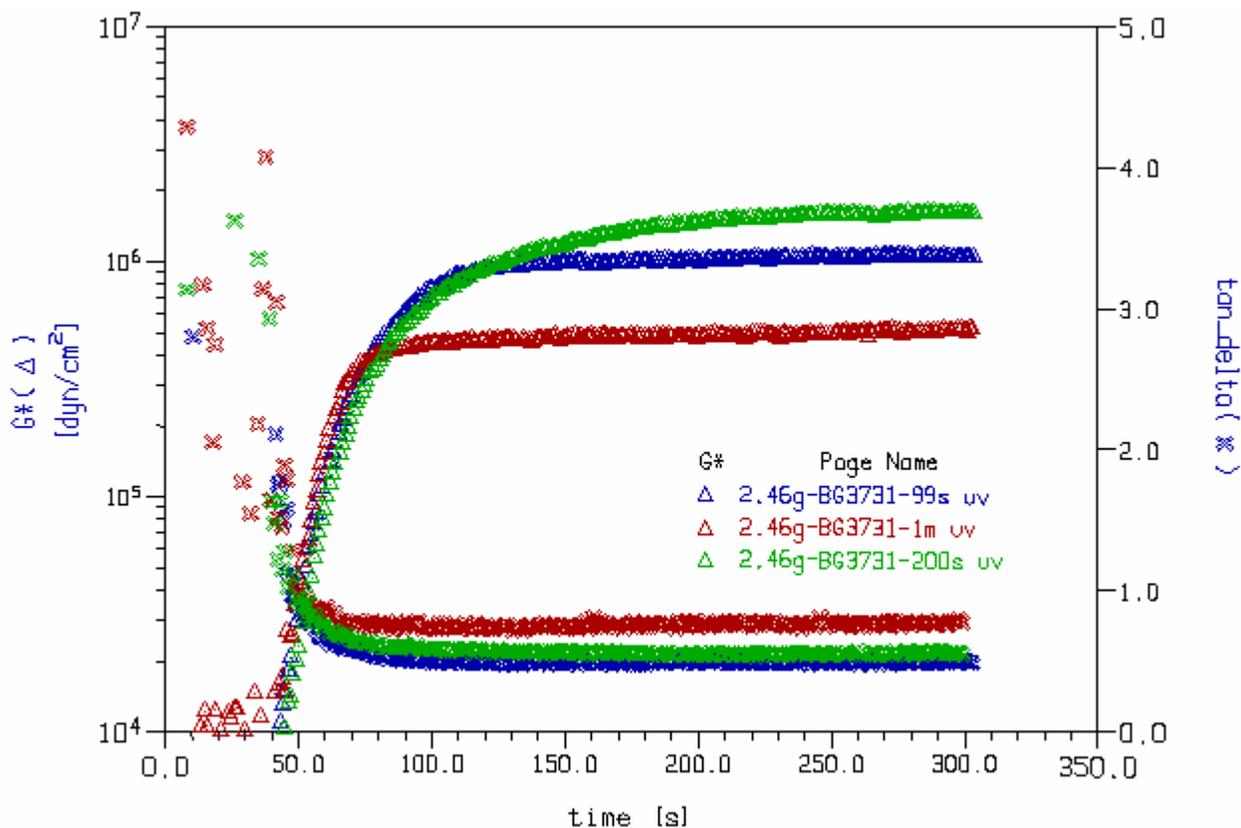
#### *Reactivity of difunctional carbene with oligomer A*

The oligomer chosen for this study (oligomer A) was an aliphatic urethane acrylate of undisclosed molecular weight. Before addressing the rheological characteristics of the reaction, UV-Vis spectroscopy was again employed to determine if reactivity could be observed between the two components. The results of this study are portrayed in figure 5 below where the growth of a new peak in the visible region is again observed. As in the case for the small molecule study above, absolute assignment of the reaction has not been completed as of this writing, but the likely route of reaction is again by insertion of the photogenerated carbene into an N-H bond.



**Figure 5: UV-Vis spectra for reaction of 3 with Oligomer A**

The oligomer and the reaction mixture of 7 and 8 were dissolved in acetone and placed in a parallel plate rheometer with an attached spot cure apparatus. This method allowed the progress of the light catalyzed reaction to be followed by monitoring the complex viscosity  $G^*$  (and as a result  $G'$  and  $G''$  values), as well as the  $\tan \delta$  value. A typical value used for establishing the formation of a three dimensional crosslinked network is the point at which the  $\tan \delta$  equals one. The plot from this reaction is shown in Figure 6 below and demonstrates that [a] gel formation occurs at approximately 50 seconds and continues decreasing (i.e. increasing storage modulus) for the remainder of the experiment.



**Figure #6: Complex Viscosity curve for reaction of Oligomer A and 7/8 mixture.**

With the ability to form a gel being demonstrated rheologically, the question remains whether the observed gel point is fact due to oligomer crosslinking facilitated by the difunctional carbene, or rather to some heretofore undescribed light catalyzed reaction of the oligomer, or possibly from self reaction of the carbene molecule with itself. These questions were addressed by irradiating solutions in acetone of the TMFPA-COOH by itself and oligomer by itself in the rheometer under the same conditions as used for the co-reaction. In both cases no crossover of the storage and loss moduli were observed, nor was significant viscosity build apparent. As in the case of the model systems, chemical characterization of the (oligomer//7/8 mixture) reaction products are on-going, as are solution studies to determine gel crosslink density and swell characteristics.

*Reaction of 3 in the presence of free radical UV formulations(Consistent formatting with previous headings)*

As may be apparent from the preceding sections, the rate of reaction of our carbene crosslinker molecule is many times slower than that seen for a typical UV cure urethane acrylate coating using phosphine oxide photo-initiators or other commercially available photo-initiators. A question still remained as to whether the addition of the carbene to a typical UV cure urethane acrylate would have any effect, either advantageous or deleterious, on the performance of the coating before, during, and after cure. Our curiosity in this area was also due to a report where di-azirine molecules also functioned as traps for carbon centered radicals.<sup>8</sup> The products 7 and 8 were dissolved in a urethane

acrylate formulation containing a bis-acylphosphineoxide photoinitiator. The mixture was exposed to UV light in the rheometer as described earlier. In this case no visible difference in final viscosity or rate of gelation could be observed in the carbene containing formulation when compared to the control formulation.

### Summary

It has been demonstrated that stable di-functional carbene molecules may be synthesized from commercially available materials and used to generate crosslinked gels of urethane/acrylate oligomers (as determined by parallel plate rheometry) in solution when exposed to UV light. The reaction is quite slow when compared to traditional UV free radical polymerization, but nevertheless reproducible. In addition, one attempt at co-reaction of the di-carbene in a urethane acrylate free radical formulation showed no observable effect in either kinetics or final properties.

### Experimental

*General Considerations:* Absorption spectra were obtained between 300 and 600 nm on a Perkin Elmer Lambda 900 UV spectrophotometer, employing either acetone, cyclohexane, or ethanol as the solvent. Mass spectra were obtained on a model Varian Saturn 2000 GC/MS connected to a Varian 3800 gas chromatograph. Rheological measurements for UV curing were performed on a Rheometrics RDA III parallel plate rheometer (8 mm diameter plates, 0.25 mm gap, frequency of 10 Hz @30% dynamic strain) with an attached Green Spot UV light source (17 mw/cm<sup>2</sup>, 0.3 ND filter, exposure time varied).

4-(1-Azo-2,2,2-trifluoroethyl)benzoic acid (Compound 3) was purchased from BaChem Calif. Inc. and N-ethylurethane was purchased from Aldrich Inc. (cat. # E5-122B) Both molecules were used as received with no further purification. All solvents were used with no additional drying and, when available, spectroscopic grade was used. Oligomer A was an aliphatic urethane oligomer obtained from Bomar Inc.

## Acknowledgements

We would like to thank Lung Wu (Corning Inc.) for his assistance in obtaining the complex rheology curves and Dr. Sue Gasper (Corning Inc.) for her help in obtaining the UV-Vis spectra.

## References

- <sup>1</sup> (a) T. H Lowry and K. Schueller Richardson,; *Mechanism and Theory in Organic Chemistry*, 2<sup>nd</sup> Edn.,; **1981**; Harper and Row Publishers NY, NY. (b) Jones, Maitland, Jr.; *Advances in Carbene Chemistry* **1994**, *1*, 161-184. (c) Moss, Robert A.; Jones, Maitland, Jr.; *Reactive Intermediates*; **1981**, *2*, 59-133
- <sup>2</sup> (a) . J.P.Collman and L.S. Hegeudus; *Principles and Applications of Organotransition Metal Chemistry*” ; **1980**, Univ. Science Book Publishers, Mill Valley, CA.
- <sup>3</sup> (a) M. T. H. Liu, ed; *Chemistry of Diazirines*, CRC Press Boca Raton, Fl; 1987. (b) R. A. Moss; *Accts. Chem. Res.*, **1989**, *22*, 15-21. (c) E. Schmitz, A. Stark; *Angew. Chem. Int'l. Ed.*, **1963**, *2*, 548
- <sup>4</sup> *IUPAC Compendium of Chemical Terminology* , 2<sup>nd</sup> edn, **1997**; describes photoaffinity as a technique whereby a molecule “...specifically associated with a biomolecule, is photoexcited in order to covalently attach a label to the biomolecule usually via intermediates.”
- <sup>5</sup>(a) J. E. Baldwin, C. D. Jesudason, M. G. Moloney, D. RhysMorgan, A.J. Pratt; *Tetrahedron*, **1991**, *47(9)*, 5603-5614. (b) A.A. Kogon, D.E. Bochkariov, B. P. Baskunov, A. V. Cheprakov; *Liebigs Ann. Chem.*, **1992**, 879-881. (c) M. Nassal; *J. Amer. Chem. Soc.*, **1984**, *106*, 7540-7545. (d) B. Erni, H. G. Khorana; *J. Amer Chem. Soc.*, **1980**, *102(11)*, 3888-3896. (d) Y. Hatanaka, M. Hashimoto, S. Nishihara, H. Narimatsu, Y. Kanaoka; *Carbohydrate Research*, **1996**, *294*, 95-108.
- <sup>6</sup> SciFinder® , copyright 2005, American Chemical Society.
- <sup>7</sup> (a) J. F. Brunner, H. Senn, F. M. Richards; *J. Biological Chem.*, **1980**, *255 (8)*, 3313-3318. (b) ref. 5-a.
- <sup>8</sup> D.H. R. Barton; J. Cs. Jaszberenyi; E. A. Theodorakis; J. H. Reibenspies; *J. Amer. Chem. Soc.*, **1993**, *115*, 8050-8059.