

region from 350 - 1000 nm, yet their temporal widths are the same as the picosecond pulses which generate them. Thus these continuum pulses constitute excellent light sources for the measurement of time resolved absorption spectra of transient intermediates produced in photochemical reactions. Experimental configurations which generate and utilize picosecond continua will be described and the results of recent experiments employing them will be presented and discussed.

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#### α9

##### Picosecond Resolution of Intersystem Crossing and Measurement of Quantum Yields in Rose Bengal

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Through the use of picosecond time resolved absorption spectroscopy, we have been able to determine the first excited singlet state lifetime of Rose Bengal, an iodinated analogue of Rhodamine 6G. We also measured the rate of ground-state repopulation. By combining these data with a literature value of the radiative lifetime, the quantum yields of intersystem crossing, internal conversion and fluorescence could be obtained without recourse to triplet quenching techniques or other secondary techniques. We suggest that this important development could find general applicability in measuring quantum yields of intersystem crossing and internal conversion.

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#### α10

##### Laser Photolysis in Globular Proteins

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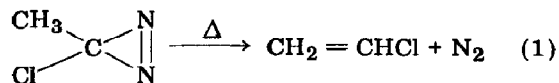
Pyrene and several derivations of pyrene are solubilized in aqueous systems by using globular proteins such as serum albumin. The pyrene atmosphere resides in various parts of the protein, but not in the aqueous phase. Laser excitation of the pyrene leads to the excited singlet and triplet state. The lifetime of the excited singlet states is dependent on the pH and temperature of the system. The changes in the lifetime reflect structural changes in the protein. Several quenchers such as O<sub>2</sub>, CH<sub>3</sub>NO<sub>2</sub>, I<sup>-</sup>, Ti<sup>+</sup> quench the excited states of pyrene in the protein. These quenchers reside mainly in the aqueous phase. The experiments thus measure the factors that affect the permeability of the protein to these quenchers. The data also give information on the nature of the protein site containing pyrene.

#### β4

##### The Photochemistry of 3-Chloro-3-Methyldiazirine

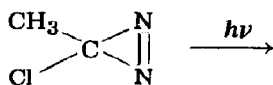
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The mechanism of thermolysis of methyl diazirines has been elucidated [1]. In the ground state the decomposition products of 3-chloro-3-methyldiazirine (I) are nitrogen and vinyl chloride.



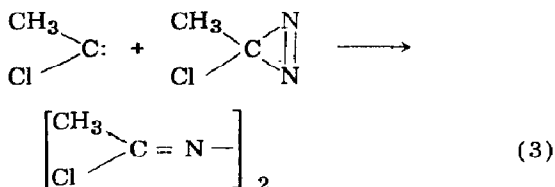
Bridge, Frey and Liu did not detect any other products [2].

The photolysis of I is known to produce [3] the products of reaction (1) as well as the fragmentation products, acetylene and hydrogen chloride [4].

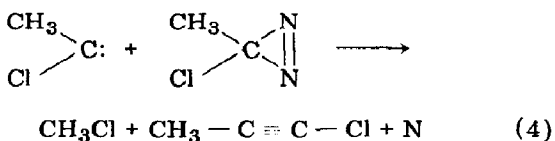


Initial results suggest that the mechanism for the photochemical reaction is similar to that proposed by Frey and Stevens for methyl diazine [5]. That is, two unimolecular channels are available from the excited state: a low energy triplet path leading to the products of reaction (1); and a singlet path with sufficient energy to form the fragmentation products.

Preliminary results suggest that bimolecular collisions between methyl chloro-carbene and the ground state of I may lead to reaction. Two reaction paths are possible. The first leads to an azine. Azines are well-known decomposition products of diazirines [6].



The second path involves elimination of nitrogen.



The fragmentation products of the photochemical reaction (2) have attracted our interest. Since the activation energy for elimination of hydrogen chloride from ground-state vinyl chloride is too high [7] to reasonably account for the yield of acetylene and hydrogen chloride, an electronically excited state of vinyl chloride is likely involved. It is well known that photolysis of vinyl chloride effects elimination of hydrogen chloride [8] which, under conditions of flash photolysis, has a sufficiently inverted vibrational population to support laser action [9].

These considerations together with the analogy of eliminations from ion-radicals analogous to methylcarbenes [10] suggest that the hydrogen chloride produced in

photolysis of I may have a significant inversion of vibrational population. Intensive efforts are under way to demonstrate this by detecting a laser pulse after flash photolysis of I.

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### $\gamma$ 6

#### Quenching of the Norrish Type II Reaction of Butyrophenone by Thiophenic Compounds

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In order to better understand the nature and energy content of the excited states of five membered heterocyclic compounds a study of quenching of the triplet state of butyrophenone by thiophenic compounds was carried out. The studies were performed in cyclohexane solutions, at 25 °C. The following quenching rate constants were determined from the Stern Volmer plots for reaction (5).

