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Dr. Alexander Greer

Department of Chemistry

Brooklyn College (USA)

President of the

American Society for Photobiology (ASP)

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Dark Processes Relevant to Reducing (or Enhancing) Photosensitized Oxidation

Very few photosensitizers function in both light and dark processes, indeed most have no function in a dark surrounding when the lights are turned off. Here, we describe a dark-binding process that is relevant to preventing photosensitized oxidation, the process is a conformation dependent light and dark reaction of a dual-functioning diketone. A conformational switch of 4,4'-dimethylbenzil for photosensitized oxidation activity and binding activity will be discussed, where the latter binds to a phosphite shutting off the sensitization. The light and dark paths are competitive, where less rotation of the diketone is better suited to the photosensitizing function since phosphite binding arises through a syn or syn-skewed conformation. The dual function seen here with the diketone is generally not available to sensitizers of limited conformational flexibility, such as porphyrins, phthalocyanines, and fullerenes..