MEDIUM EFFECTS ON THE DIRECT CIS-TRANS PHOTOISOMERIZATION OF 1,4-DIPHENYL-1,3-BUTADIENE IN SOLUTION. Christopher Redwood and Jack Saltiel Department of Chemistry and Biochemistry, Florida State University, Tallahassee, FL 32306-4390.

The interpretation of solvent effects on fluorescence quantum yields and lifetimes of trans,trans-1,4-diphenyl-1,3-butadiene (tt-DPB) has been based on the assumption that torsional relaxation leading to photoisomerization is the only radiationless process that competes with radiative decay. Measured photoisomerization quantum yields in benzene, cyclohexane, methylcyclohexane, hexane and perfluorohexane are too low to be consistent with this interpretation. Radiationless excited state pathways exist in tt-DPB which do not lead to photoisomerization. The interpretation of photophysical observations for tt-DPB in alcohols, without regard to the possible contribution of competing radiationless decay processes, is especially troubling because it is known that alcohols photoadd to tt-DPB. We have measured UV absorption spectra in the course of the irradiation of tt-DPB in methanol, ethanol and isopropyl alcohol. Analyses of the spectral matrices indicate that trans → cis photoisomerization is faster than photoaddition. Measurement of the photoreaction quantum yields in alcohols is in progress.