It is well known that in photochemical reactions there is a preparation stage ahead of the reactive encounter. For example the reactivity of triplet states results from the intersystem crossing of molecules prepared in their singlet manifold. We have studied here the ultrafast dynamics of substituted ethylenes, namely hexenes, following their excitation at 200nm. This region corresponds to their first excited singlet states where an extensive state mixing occurs between Rydberg and valence states. We have observed by time of flight mass spectrometry the decay of the initially excited states probed at 263nm. There appears a rapid decay in the 100 fs regime followed by a slower evolution ranging from 2 to 5ps. The rapid decay has been assigned to the wave packet motion connecting the Rydberg and valence states. Rydberg states have a quasi planar geometry while the valence states exhibit a 90 eclipsed configuration corresponding to the opening of the double C=C bond and rotation about it. By comparing various isomers of the hexenes, we have observed a wealth of behaviours and assigned the ultrafast evolution to the double bond opening followed by internal conversion to the ground electronic state of the system. The constrained ones or possessing heavy substituents on both sides of the double bond exhibit a longer initial decay relative to the others with a lower moment of inertia about the initial double bond. This ultrafast evolution is very similar to the rotation observed by A.H.Zewail on stilbene yielding the formation of a diradical state.