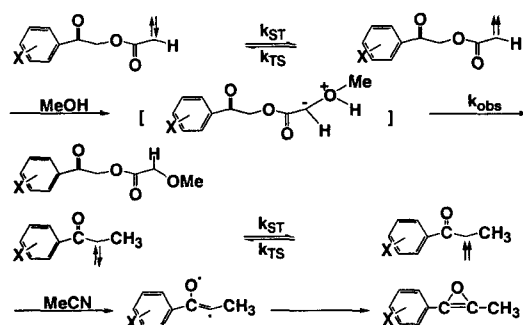


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Rate constants of photolytic reactions of carbenic ylids and radicals in various quenchers were determined under the irradiation condition of below 190nm wavelength after synthesized the corresponding precursors of the carbenes in order to investigate contribution of the substituent effect and electronic spin state on the reaction energy.



The ylid intermediate moves to the higher activated transition state, which is the step of proton migration. The photochemical reaction of aromatic ketocarbenes in acetonitrile gives a radical intermediate and forms a new O-C bond at the transition state.

The thermodynamic activation parameters give an important criterion to analysis the mechanism of carbenic intermediates: The  $\rho^{\ddagger}$ -value indicates to develop the positive charge at the carbonyl oxygen center.

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