Substituent Effect in the Photolysis of *p*-Substituted Phenyldiazirines in the Presence of Carbone Monoxide

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Irradiation (λ) 478nm) of p-substituted phenyldiazirines was carried out in argon matrix and products were isolated in the matrix. The argon matrix was deposited on cesium iodide for the infrared spectrum and on sapphire for the ultraviolet spectrum at 10K. The C-H deformations of the phenyl group are changed very little in going from arylazirine to phenyldiazomethane and then finally phenylmethylene as is corresponding to the C-H deformation mode of the methane hydrogen at 445cm⁻¹. The indentity of phenylmethylene was confirmed by an experiment in an argon matrix doped with 0.25% carbon monoxide. The observed rate constants of carbene abstraction with carbon monoxide showed high in the case of electron-donating substituents. The reactivity magnitude, ρ -value showed high positive value, that is, the electron donating substituen -ts are retarded insertion of carbon monoxide, while the electron-withdrawing substituents accelerate the insertion reaction. The electron donor groups on phenyl ring destabilize the negative charge on the carbenic carbon and raise the transition state energy.