tert-Butylcyanoketene-substituted styrene cycloadditions. A kinetic study

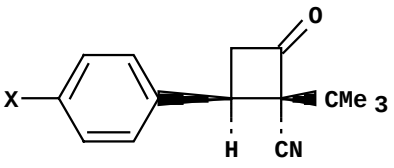
Prof. SHAIKH ASROF ALI

Dept. of Chemistry , College of Science ,
King Fahd University of Petroleum & Minerals

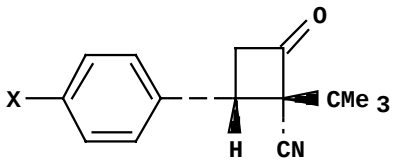
http://www.kfupm.edu.s

ABSTRACT

Rate consts. for the cycloaddn. of Me3CC(CN):C:O (I) with 4-XC6H4CH:CH2 (X = H, Me, Me3C, MeO, Br) at different temps. have been detd. by 1H NMR spectroscopy. The addn. reaction afforded contra-thermodn. adducts (II) stereoselectively; a way has been found to convert II into thermodn. cyclobutanones (III). The activation parameters of the cycloaddns., along with the Hammett reaction const. and the solvent effect on cycloreversion of II, indicate a concerted asynchronous mechanism involving a transition state with some degree of charge sepn. An approx. difference in the energy of activation between the favorable and unfavorable mode of I-p-methoxystyrene addn. has been detd. to be 10.6 kJ mol-1.



II



III