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BROMINATION OF CINNAMYL HALIDES, AND RELATED STUDIES

A thesis presented to
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for the Degree of

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by

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ABSTRACT

The rates of bromination of the (E)-cinnamyl halides in acetic acid have been measured so that the electronic effects of a halomethylene group on a π system might be better understood. The relative rates of bromination decrease in the order $PhCH{=}CHCH_2F$ > $PhCH{=}CHCH_2Cl$ > $PhCH{=}CHCH_2Br$. Rate constants could not be calculated from the kinetic data and reasons for this are discussed in great detail. The earlier literature proposal that this reactivity order was due to hyperconjugation of the C-H bonds of the $-CH_2X$ group is shown to be incorrect, and new explanation is proposed in terms of modern molecular orbital theory.

A detailed study of the products of bromination of the (E)-cinnamyl halides in acetic acid under the conditions of kinetic measurement is also reported. Product precursors, consistent with the products observed, have been tentatively identified.

Several $[\alpha,\alpha\text{-}{}^2H_2]$ - cinnamyl derivatives, $PhCH{=}CHCD_2X$, have been prepared and the addition of several electrophiles to these alkenes has been studied.