



"DEUTERIUM AND CARBON ISOTOPE EFFECT STUDIES
OF
THE McLAFFERTY REARRANGEMENT
OF
SUBSTITUTED BUTYROPHENONES"

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SUMMARY

The objective of the work reported in this thesis was to elucidate the details of the mechanism for the loss of ethylene from molecular cations of various substituted butyrophenones; i.e., the McLafferty rearrangement. Mechanisms proposed for the rearrangement are, (i) stepwise, with hydrogen transfer as the rate determining step, (ii) stepwise, with carbon-carbon bond cleavage as the rate determining step and (iii) concerted.

The approach used in this investigation was to study possible isotope effects for the ion source and first field free region decompositions of 4-($^2\text{H}_1$)-*p*-substituted butyrophenones and 4-($^2\text{H}_1$)-2-ethyl-*p*-substituted butyrophenones. Deuterium isotope effects were observed for both series of compounds. Trends observed in the isotope effect with Brown's σ_p^+ values are discussed in terms of Westheimer's theory. The possibility that 1,5-hydrogen migration in these systems is an equilibrium situation is also discussed.

In addition, 1-(^{13}C)-butyrophenone, 2-(^{13}C)-butyrophenone, 3-(^{13}C)-butyrophenone and 4-(^{13}C)-butyrophenone were prepared and attempts were made to measure intermolecular carbon-13 isotope effects for loss of ethylene from these compounds. The difficulties involved in such measurements are discussed.

Compounds 3-(^{13}C)-2-ethylbutyrophenone and 4-(^{13}C)-2-ethylbutyrophenone were synthesized and a carbon-13 isotope effect was measured for the field free region reaction of the former. The carbon-13 and deuterium isotope effects and the observation of an α -secondary isotope effect for the reaction of 3-($^2\text{H}_2$)-2-ethylbutyrophenone are discussed in terms of the possible mechanisms for the process.

Deuterium and carbon-13 isotope effects were calculated using various reactant and transition state models based on the stepwise and concerted mechanisms proposed. The results obtained from the concerted models were shown to reproduce the experimental isotope effects, at least in a semi-quantitative fashion.

Experiments were performed in an attempt to detect the presence of an intermediate in the reaction pathway. Clearly, the existence of such a species precludes the possibility of the operation of the concerted mechanism for the McLafferty rearrangement in this system. Ion-molecule reactions of 4-(²H₂)-butyrophenone were investigated but the presence of such an intermediate could not be observed. 2-Allylbutyrophenone was prepared in order to provide an alternative pathway to the McLafferty rearrangement for the proposed intermediate. The mass spectrum of this compound is discussed.