

Book review

Advances in Carbocation Chemistry, Vol. 2, J.M. Coxon (ed.), JAI Press, Greenwich, CT, 1995, ix + 273 pp., £62.50, US\$97.50, ISBN 0-89232-952-1.

This volume contains six reviews as follows: The formation of carbon-carbon bonds via benzylic-cation-initiated cyclization reactions (S.R. Angle and H.L. Mattson-Arnaiz); Application of one-bond carbon-hydrogen NMR coupling constants to the determination of the structure of carbocations in superacids (D.P. Kelly); Strained bridgehead cyclobutyl cations (E.W. Della and C.H. Schiesser); Structure, bonding, and electron-delocalization modes in observable "classical" tertiary carbocations (T.S. Sorensen); Nucleophilic substitution and solvolysis of simple secondary carbon substrates (P.E. Dietze); Electrophilic aromatic nitration via radical cations: feasible or not? (L. Ebersson, M.P. Hartshorn, and F. Radner). All are by active contributors to the respective fields, and the overall standard of presentation is high; importantly, the authors make critical analyses and judgements rather than simply listing the experimental observations and competing hypotheses. Especially valuable are the 'Conclusion' sections at the end of the reviews. I found that reading these sections first significantly lightened the task of going systematically through the detail.

Of particular interest to some Main Group organometallic chemists, in view of much current activity in the field of silylium ions and related derivatives of Ge, Sn, and Pb, will be the authoritative and very well organized account of the structures of 'classical' tertiary ions by T.S. Sorensen. In spite of high level calculations carried out by Schleyer, the lowest energy form even of

the *t*-butyl cation is not unambiguously established, but it seems fairly certain that it can be described as essentially planar, with C-H hyperconjugation very important for the stability. For the more complex ions discussed there are often only very small differences in energy between the various possible forms, including unbridged ions and ions bridged by alkyl groups or hydrogen atoms, and in some cases the classical structure is a transition state! Professor Sorensen concludes his account with the words: "Classical cations are dead! Long live research on classical cations."

It begins to look at last, after some 60 years of competing hypotheses (my own introduction to the topic came 54 years ago during undergraduate lectures given by E.D. Hughes himself), that the mechanism of solvolyses of simple secondary carbon halides, tosylates, etc., may have been settled. They are, it appears, just S_N2 processes with a highly unsymmetrical transition state. An important point emphasized in this account, and one that I find overlooked in a significant proportion of papers dealing with organometallic mechanisms, is that characterization of transition state does not prove the existence of an intermediate.

This book is modestly priced on present day standards and should be in the library of all institutions concerned with organic chemistry.

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