Prof. Theodore S. Sorensen

A Tribute

on the occasion of his 75th birthday

Theodore S. Sorensen was born in the Peace River Country of Northern Alberta, Canada, on June 6, 1934. He received his B.Sc. with first class Honors in Chemistry from the University of Alberta in 1956. His first taste of research came during summer research positions at the Defense Research Board Laboratories in Dartmouth, Nova Scotia in 1955 and Shirley Bay, Ontario, in 1956. Ted pursued graduate studies in Chemistry, enrolling in the Ph. D. program at the University of Wisconsin. He worked under the supervision of Edward M. Kosower on the synthesis of 1,2- and 1,4-dihydropyridines and received his Ph.D. degree in 1960. He was then awarded the prestigious three year I.C.I. Fellowship for postdoctoral studies with Professor C. Eaborn at the University of Leicester. After the second year, he accepted an offer of a position as Assistant Professor at the fledgling University of Calgary, and rose rapidly through the ranks, becoming Full Professor in 1973. He held visiting professorships at Canterbury University (1967) Australian National University (1971-2), University of Sussex (1978-9) and University of Erlangen (1979). He is a member of the American Chemical Society and the American Association for the Advancement of Science, and a Fellow of the Chemical Institute of Canada. He has been a member of the Editorial Advisory Board of the Canadian Journal of Chemistry (1979-81), and served on the organizing committee of numerous national and international conferences

The synthesis, and kinetic, thermodynamic, stereochemical, and spectroscopic studies of electron deficient compounds, and carbocations in particular, have had a profound impact on understanding all aspects of chemical structure and reactivity in organic chemistry as recognized by the award of several Nobel Prizes. Ted Sorensen has many outstanding and seminal contributions in the area of carbocation chemistry over the last forty years. He had discovered and demonstrated the stereochemistry of pericyclic reactions in divinyl carbocations a few years before Woodward and Hoffmann became household names. His work on the mechanisms of rearrangements of numerous carbocations and specifically norbornyl cations, and the fluxional

behaviour of cyclopropylcarbinyl cations, played a key role in resolving correctly the long-standing classical *vs* non-classical controversy of carbocation structure. He was the first to discover hydrido-bridged cations. These are novel systems whose basic structure may be regarded as a hydride *anion* sandwiched between and stabilized by *two* cationic centers. Ted Sorensen's discovery of these systems, and elucidation of their structure and bonding has broad implications on the chemical reactivity of supposedly inert C-H bonds under Lewis acidic conditions as occurs in many guises in the fields of organic and organometallic chemistry, not to mention catalysis in the petrochemical industry. He demonstrated and explained the unique role of cyclopropyl groups in the stabilization of electron-deficient sites. There are no fewer than ten citations in March's, *Advanced Organic Chemistry*, the bible of organic chemistry, on this and other aspects of his carbocation studies. Discoveries of distinct conformations in apparently simple structures such as 2-adamantyl and 1-cyclohexyl cations will have similar impact in a much broader context. In short, his work in the field of carbocation chemistry continues to refine, even redefine, structural thinking in organic chemistry.

A long-standing interest in organometallic carbocationic systems has led to his discovery of a versatile class of nucleophiles and a new method for the synthesis of ketenes and cyclopropanones, including a first observation of a bicyclo[1.1.0]butanone. Ted Sorensen has discovered that these bicyclic ketones and certain substituted cyclopropanones have strongly pyramidal carbonyl groups, a discovery which has ramifications for explaining and predicting the stereochemistry of arguably the single most important reaction class in organic chemistry, nucleophilic addition to carbonyl compounds.

Ted Sorensen's research is characterized by numerous other important contributions to a solid foundation for scientific enquiry, among them, refinement of superacid/nmr techniques for the observation of reactive intermediates, nmr kinetic studies of hidden exchange processes and molecular rearrangements, new techniques for the *in situ* preparation of reactive species, and examination of the chirality and aromaticity of arene metal tricarbonyl and related complexes. At all stages his research has been supported by detailed studies of structures and mechanisms by high-level theoretical calculations.

Ted Sorensen has been internationally recognized in the form of a feature article in Accounts of Chemical Research, six invitations to write book chapters and numerous invitations to speak at International conferences. Sorensen is very worthy of a commemorative issue of ARKIVOC.

Silvio Buscemi

Selected Publications

1. Sorensen, T. S. The synthesis and reactions of divinyl carbonium ions. *Canad. J. Chem.* **1964**, *42*, 2768.

2. Sorensen, T. S. The preparation and properties of some methyl-substituted heptatrienes. *Canad. J. Chem.* **1964**, *42*, 2781.
3. Sorensen, T. S. The preparation and reactions of a homologous series of polyenic cations. *J. Amer. Chem. Soc.* **1965**, *87*, 5075.
4. Olah, G. A.; Pittman, C. U.; Sorensen, Jr. and T. S. Pentadienyl cations and their rearrangements in FSO_3H-SbF_3 solution. *J. Amer. Chem. Soc.* **1966**, *88*, 2331.
5. Price, J. T.; Sorensen, T. S. Nuclear magnetic resonance study of arene metal tricarbonyl complexes. *Canad. J. Chem.* **1968**, *46*, 515.
6. Sorensen, T. S.; Ranganayakulu, K. Cyclopropylcarbinyl-allyl cation rearrangements. *Tetrahedron Lett.* **1970**, 659.
7. Sorensen, T. S.; Jablonski, C. R. Organometallic carbonium ions. NMR studies of cis and trans-pentadienylirontricarbonyl cations. *J. Organomet. Chem.* **1970**, *25*, C62.
8. Huang, E.; Ranganayakulu, K.; Sorensen, T. S. Observable degenerate rearrangements in 2-methyl-2-norbornyl and related cations. *J. Amer. Chem. Soc*. **1972**, *94*, 1780.
9. Sorensen, T. S.; Miller, I. J.; Ranganayakulu, K. Stabilization of an adjacent carbocation center by cycloalkyl groups. The uniqueness of cyclopropyl. *Austral. J. Chem.* **1973**, *26*, 311.
10. Rajeswari, K. and Sorensen, T. S. The rearrangement of cyclopropyl-substituted allylic cations II an intramolecular 2 + 2 cycloaddition. *J. Amer. Chem. Soc.* **1973**, *95*, 1239.
11. Huang, L.; Ranganayakulu, K.; Sorensen, T. S. Cycloallyl-bicycloalkyl cation interconversions. *J. Amer. Chem. Soc.* **1973**, *95*, 1936.
12. Cone, R.; Haseltine, R. P.; Kazmaier, P.; Sorensen, T. S. Degenerate rearrangements in a cyclohexenyl cation. independent ring carbon interchange and hydrogen interchange processes. *Canad. J. Chem.* **1974**, *52*, 3320.
13. Haseltine, R.; Huang, E.; Ranganayakulu, K.; Sorensen, T. S. The observable thirtyfold degenerate camphenehydro cation. A stereospecific exo-3,2-methyl shift and endo-6,2 (exo 6,1)-hydride shift. *Canad. J. Chem.* **1976**, *53*, 1056.
14. Sorensen, T. S. Terpene rearrangements from a superacid perspective. *Acc. Chem. Res.* **1976**, *9*, 257.
15. Kirchen, R. P.; Sorensen, T. S. The methylcyclobutyl cation. A simple sp^3-hybridized carbocation? *J. Amer. Chem. Soc.* **1977**, *99*, 6687.
16. Kirchen, R. P.; Sorensen, T. S. conformational analysis of tertiary cyclo-alkyl (C_6, C_7, C_8) carbocations. Unexpected preference for the twist boat conformation in the cyclohexyl case. *J. Amer. Chem. Soc.* **1978**, *100*, 1487.
17. Okazawa, N.; Sorensen, T. S. The lineshape analysis of NMR peaks broadened by the presence of a "hidden" exchange partner. *Canad. J. Chem.* **1978**, *56*, 2737.
18. Kirchen, R. P.; Sorensen, T. S. The 1,6-dimethylcyclodecyl cation. Evidence for a 1,6-μ-hydrido structure. *J. Chem. Soc., Chem. Commun.* **1978**, 769.
19. Kirchen, R. P.; Sorensen, T. S. Ring size limits for the direct observation of hydrido-bridged secondary cycloalkyl cations. Correspondence with chemical reactivity studies. *J. Amer. Chem. Soc.* **1979**, *101*, 3240.

20. Schmitz, L. R.; Sorensen, T. S. The energy separation between secondary and tertiary bicyclo [2.1.1]hexyl cations. Partial bonding in carbocation structures. *J. Amer. Chem. Soc.* **1980**, *102*, 1645.
21. Kirchen, R. P.; Ranganayakulu, K.; Rauk, A.; Singh, B. P.; Sorensen, T. S. Dimethyl-cyclodecyl cations. The evidence for μ-hydrido-bridging. *J. Amer. Chem. Soc.* **1981**, *103*, 588.
22. Schmitz, L. R.; Sorensen, T. S. Nortricyclylcarbinyl carbocations - structural hybrids of cyclopropyl-carbinyl and bridged 2-norbornyl carbocations. *J. Amer. Chem. Soc.* **1982**, *104*, 2600.
23. Okazawa, N. E.; Sorensen, T. S. Solution carbocation stabilities measured by internal competition for a hydride atom. *Canad. J. Chem.* **1982**, *60*, 2180.
24. Sorensen, T. S. A near perfect complementarity of equilibrium isotope effects. A corrected value for a recently published equilibrium constant derived for the $h_{10}d_1$-2-norbornyl cation. *J. Org. Chem.* **1984**, *49*, 4310.
25. Kirchen, R. P.; Sorensen, T. S.; Wagstaff, K.; Walker, A. M. The characterization of and the evolution of molecular hydrogen by the μ-hydrido-bridged cyclodecyl cation. Relevance to the question of hydrocarbon protonation by superacids. *Tetrahedron* **1986**, *42*, 1063.
26. Kirchen, R. P.; Ranganayakulu, K.; Sorensen, T. S. 1-Methyl-1-cyclohexyl carbocations - equilibrium in search of structures. *J. Amer. Chem. Soc.* **1987**, *109*, 7811.
27. Finne, E. S.; Gunn, J. R.; Sorensen, T. S. Evidence for equilibrating 'structures' in unsymmetrical tertiary 2-adamantyl cations - possible pyramidal distortion of observable solution carbocations. *J. Amer. Chem. Soc*. **1987**, *109*, 7816.
28. Masters, A. P.; Sorensen, T. S.; Ziegler, T. A Theoretical study of ketene forming reactions involving halogen abstraction by metal carbonyl anions. *Organometallics* **1989**, *8*, 1088.
29. Masters, A. P.; Sorensen, T. S. Low temperature ketene preparations using nitrosyltetracarbonylchromium(-II) anion. *Tetrahedron Lett.* **1989**, *30*, 5869.
30. Dutler, R.; Rauk, A.; Sorensen, T. S.; Whitworth, S. M. An ab initio molecular orbital study of the 2-adamantyl cation. *J. Amer. Chem. Soc*. **1989**, *111*, 9024.
31. Masters, A. P.; Sorensen, T. S. The preparation and reactions of ω-bromoacylmanganese pentacarbonyls. *Canad. J. Chem.* **1990**, *68*, 502.
32. Sorensen, T. S.; Whitworth, S. M. A study of the stereochemical factors involved in multistep 1,2-hydride transfers. *J. Amer. Chem. Soc*. **1990**, *112*, 6647.
33. Sorensen, T. S.; Whitworth, S. M. μ-Hydrido-bridging in tricycloalkyl carbocations. *J. Amer. Chem. Soc.* **1990**, *112*, 8135.
34. Buffam, D. J.; Sorensen, T. S.; Whitworth, S. M. A study of the observable axial and equatorial-2,4-dimethyl-2-adamantyl cations. Further examples of equilibrating nonclassical structures in ordinary tertiary carbocations. *Canad. J. Chem.* **1990**, *68*, 1889.
35. Kirchen, R. P.; Sorensen, T. S.; Whitworth, S. M. A mechanistic study of the carbocation route from tetrahydrodicyclopentadiene to the adamantane ring. *Canad. J. Chem.* **1993**, *71*, 2016.

36. Sorensen, T. S.; Sun, F. Stereospecific synthesis of hindered cis-disubstituted cyclopropanones. fluxional cyclopropanones. *J. Amer. Chem. Soc.* **1995**, *117*, 5592.
37. Rauk, A.; Sorensen, T. S.; Sun, F. Preparation and structure investigations of simple bicyclo[1.1.0]butanones. *J. Amer. Chem. Soc.* **1995**, *117*, 4506.
38. Rauk, A.; Sorensen, T. S.; Maerker, C.; Carneiro, J. W. de M.; Sieber, S.; Schleyer, P. v. R. The axial and equatorial 1-methyl-1-cyclohexyl cation isomers both have chair conformations but differ in c-c and c-h hyperconjugation modes. *J. Amer. Chem. Soc.* **1996**, *118*, 3762.
39. Hrovat, D. A.; Rauk, A.; Sorensen, T. S.; Powell, K.; Borden, W. T. Ring opening of bicyclo[n.1.0]alkanones to 2-cycloalkanon-1,3-diyls. Why does oxyallyl diradical formation require less energy from bicyclo[3.1.0]hexan-6-ones than from bicyclo[1.1.0]butan-2-ones? *J. Amer. Chem. Soc.* **1996**, *118*, 4159.
40. Sorensen, T. S.; Sun, F. An oxyallyl (or oxyallyl-like) geometry is a key structure in the reaction of ketenes and diazoalkanes to form cyclopropanones. *J. Amer. Chem. Soc.* **1997**, *118*, 11327.
41. Sorensen, T. S.; Sun, F. Fluxional cyclopropanones. Approaching measurable equilibrium concentrations of acyclic oxyallyls. *J. Chem. Soc. Perkin 2* **1998**, 1053.
42. Filippi, A.; Trout, N.A.; Brunelle, P.; Adcock, W.; Sorensen, T. S.; Speranza, M. Origin of diastereofacial selectivity in tertiary 2-adamantyl cations. *J. Amer. Chem. Soc.* **2001**, *123*, 6396.
43. Rauk, A.; Sorensen, T. S.; Schleyer, P. von R. Tertiary cyclohexyl cation. Definitive evidence for the existence of isomeric structures (hyperconjomers). *J. Chem. Soc, Perkin Trans. 2* **2001**, 869.
44. Taeschler, C.; Sorensen, T. S. A deepseated carbodication rearrangement. Limited paths because of charge repulsion. *Tetrahedron Lett.* **2001**, *42*, 5339.
45. Adcock, W.; Trout, N. A.; Vercoe, D.; Taylor, D. K.; Shiner, V. J.; Sorensen, Jr. and T. S. Solvolysis of (Z)-5-trimethylstannyl-2-adamantyl p-bromobenzene sulfonate: mechanistic implications of a record-breaking secondary α-deuterium kinetic isotope effect for an S_N1 substrate. *J. Org. Chem.* **2003**, *68*, 5399.
46. Bhargava, S.; Hou, J.; Parvez, M.; Sorensen, T. S. Preparation and crystal structure of two bicyclo[1.1.0]butan-2-ones: a hybrid oxyallyl-cyclopropanone motif. *J. Amer. Chem. Soc.* **2005**, *127*, 3704.
47. Fraschetti, C.; Novara, F.R.; Filippi, A.; Trout. N.A.; Adcock, W.; Sorensen, T. S.; Speranza, M. Gas-phase diastereoselectivity of secondary 5-substituted (x)-adamant-2-yl (X=F,$Si(CH_3)_3$) cations. *J. Org. Chem.* **2007**, *72*, 4077.
48. Hamblin, G.D.; Jimenez, R.P.; Sorensen, T. S. A Theoretical study of Favorskii reaction stereochemistry. Lessons in torquoselectivity. *J. Org. Chem.* **2007**, *72*, 8033.