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Foreword

Dedication to Professor Roger F. C. Brown

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Roger Brown died on 1 September 2013 after a lifetime of developing new organic chemistry, nearly all of which was published in *Aust. J. Chem.*, and it is fitting that the Journal is paying tribute to his contributions (Fig. 1).

Roger Brown's patronymic heritage stems from his great-grandfather, George Brown (1835–1917), Wesleyan Missionary, author and explorer in the Pacific Islands, who settled in Sydney in 1880. George's daughter, Elizabeth, established an academic ideal for the family, completing a B.A. at Sydney University in 1885. George's son, Frederick Brown worked in real estate in the early 1900s when the North Shore was being subdivided after the railway had been opened. He established a comfortable home in Chatswood where his son, Herbert Brown (1898–1971), played tennis with his future bride, Ruth Carver (1899–1981). Roger's father, Herbert, did his schooling at Shore and, in 1917, went to the new Wesley College at Sydney University, but enlisted and was embarked for France when World War I ended abruptly and the ship did not sail. He completed his B.A. in 1921, taught for two years and went to Oxford to study history in 1923. He returned in 1925 and, in 1926, married Ruth, Roger's mother, who in the meantime had trained as a nurse. Unsettling experiences in teaching ended as the Depression began, and Herbert used his writing skills to earn a living in advertising. Herbert brought to the family a delight in academic study, while Ruth brought a strong ambition for the future careers of her three sons in better economic times.

Fig. 1. Roger Brown.

Roger Brown was born in 1931 and had two younger brothers, Jules (1936) and Michael (1938–1997). Being somewhat older than his brothers, he had to find friends and enthusiasms outside the family. As the boys grew, they were encouraged to follow their own interests: Roger, at age 14, had come across organic structural formulae in an old text and developed an interest in chemistry – he set up his own laboratory and continued to make model aeroplanes, a lifetime hobby; Julian had engineering interests, and he later studied physics and became a physical chemist; Michael, the future rebellious artist, kept bees. In succession, they attended Shore (Sydney Church of England Grammar School) which was begun in 1889 and took the motto *'Vitai Lampada Tradunt'* ('They hand on the torch of life'), a quote from Lucretius. The poem, *'Vitai Lampada'*, written by Sir Henry Newbolt in 1892, used widely in Australian schools in the early 20th century and familiar for its refrain 'Play up, play up and play the game', expounded the selfless commitment to duty expected of each new generation of young men.[1] Sport, the Empire, the classics, and established religion had been the 19th century formula for expansion. The attitudes engendered by such training were severely dented by World War I and became decidedly unappealing at the end of World War II, when colonial empires were about to contract. Nevertheless, the school provided an excellent education and Roger did exceptionally well in chemistry and, although not achieving the result he hoped for in English, his originality and ability were demonstrated convincingly by having three poems published in the Sydney Bulletin in 1950–51.

Sydney University, when Roger attended in 1949, was a much wider world than that previously encountered, where people struggled to understand what had led to the horrors of the previous decade and why the world was again dividing on

Frank Eastwood was Reader in Chemistry at Monash University and retired in 1995. Born in 1930, he went to North Sydney Boys High School and enrolled at Sydney University in 1948 and completed his B.Sc. (Hons) in 1952 and M.Sc. in 1954. He worked with Sir Robert Robinson in Oxford for his D.Phil. and in 1956 moved to Cambridge to work with Sir Alexander Todd on antibiotics. He was appointed to Monash University in 1960 and helped initiate teaching in 1961. He collaborated with Roger Brown on pyrolysis from 1972 until 1995.

ideological grounds; where Andersonian philosophy[1] questioned all moral precepts; and where science, in high repute from its wartime successes, required much time and effort for its study. In higher years, the chemical laboratories were open for long periods, and experimental skills could be developed. In chemistry lectures, there was fledgling theory and much analogy. Training in research in chemistry began with projects in third year and continued through the Honours year. There was paper chromatography, but column chromatography was not yet in use; purification of solvents was a necessary ritual; spectroscopy was limited to a non-recording UV/vis spectrometer; and structural evidence came from chemical behaviour and derivatives. Skill in isolating crystalline compounds was necessary, and the excitement came when the percentage figures for the elemental analyses arrived and when compounds formed from different routes could be shown to be identical. As today, students who understood the processes of research could arrive at the research front in four years. As today, students appreciated that nobody knew all the answers and that if you thought something was wrong, you had first to produce convincing evidence for an alternative interpretation.

From his Honours year in 1953 until his arrival in Canberra in 1961, Roger worked in collaboration with others. His first project with G. K. Hughes and E. Ritchie was the isolation of natural products from a plant species as part of the Australian Phytochemical Survey for which he was awarded first class Honours and the University Medal. His M.Sc. research involved reinterpretation of previous experimental results and some defining experiments to arrive at the correct structure of the alkaloid Flindersine as well as other work. He was awarded an 1851 scholarship and went to Cambridge University in 1955 to do a Ph.D. degree with Sir Alexander Todd (later, 1961, Lord Todd) under the immediate supervision of Malcolm Clark. The project involved development of the chemistry of nitrones for the synthesis of corrin, the central framework of vitamin B12. Two American post-doctoral students, Ronald Breslow and Murray Goodman, later distinguished professors, brought to Cambridge intense discussions on mechanism using curly arrows to show the electron accounting and precise valency of each element. Clark, who had spent some time with R. B. Woodward, also expounded chemistry with precise structures in proposing syntheses, and Woodward himself filled blackboards with his beautiful completed syntheses during his visits. In this way, the new approaches to theory were spread to those trained in interpretation rather than prediction. The availability of instruments was increasing at this time, with recording infrared and ultraviolet spectrometers and the first 40 Mhz NMR machines now in use. Column chromatography was now a widely used technique. The 1950s was also a period when chemists were thinking about mechanisms more deeply, and new reactive intermediates were being hypothesised.

In 1957, Roger attended a conference in Glasgow where George Büchi of MIT opened the eyes of the audience to the insights that could be obtained by a combination of spectroscopy and degradative and synthetic chemistry. After completion of his Ph.D., Roger, newly married to Mary Glasscock, joined the Büchi laboratory for a year's post-doctoral study. Here, Roger used his expertise in N-oxide and related chemistry to open a new degradative route which led finally to the structure of the alkaloid aconitine. In Büchi's laboratory, thermal cracking of β-keto *tert*-butyl esters by dripping them through a hot packed column was used routinely to prepare ketones. In addition, the key references to the early literature of pyrolysis

Fig. 2. Roger Brown spent his lifetime developing new organic chemistry, nearly all of which was published in *Aust. J. Chem.*

were available.[2] Roger returned to his Christ's College Fellowship in Cambridge for a short time and took up a Lectureship, later Senior Lectureship, in the School of General Studies in Canberra in 1961 (Fig. 2).

In colleges and laboratories in Sydney University, Cambridge University and MIT, Roger made lifelong friendships with colleagues, some of whom continued in academic chemistry and with whom he collaborated in later years. As his own career developed, he made a point of meeting those researchers from around the world who were advancing fields closely related to his own and many of them became friends.

Roger's first papers reported results from experiments arising from his previous studies, and he continued to develop nitrone chemistry. In 1964, Roger's colleague at the School of General Studies, W. D. (Bill) Crow, purchased an electrically heated Lindberg tube furnace, which was used by his M.Sc. student, Richard K. (Dick) Solly, in some of the first investigations of preparative vacuum pyrolysis of organic compounds, at first by dripping a benzene solution of ninhydrin (indanetrione) down a heated tube (to form benzyne), but soon modified to flash vacuum pyrolysis (FVP) (or flash vacuum thermolysis (FVT)), whereby the starting material was sublimed through a loosely packed or empty tube and the product collected on a cold-finger condenser.[3] Such reactions were controlled by the temperature of the tube and the rate of sublimation. The idea was to use starting materials which would fragment to give one or more very stable, small molecules and, through elimination, create a highly reactive intermediate which would then rearrange and yield isolable compounds. Carbon monoxide and carbon dioxide were the initial choice for the fragments to be lost, as there was growing evidence for their loss from radical cations in mass spectra. In collaboration with J. F. W. McOmie of Bristol, the work was extended to phthalic anhydride as a source of benzyne.[4] A range of acid anhydrides and carbonyl compounds including heterocyclic derivatives were studied and details of the processes defined. At the same time, others around the world, namely, M. P. Cava, E. K. Fields, and S. Meyerson were beginning or developing related studies.

In 1968, Roger accepted an appointment to a Readership at Monash University and continued to develop his research. His success over the years led to his appointment to a Personal Chair in 1992.

An increase in the variety of reactive intermediates came in 1972 with a project in which methyleneketene (propadienone) was the objective. Roger searched for a rational thermal fragmentation that would give ketenes and small stable molecules which, under the experimental conditions, would be lost from the system. He came across the chemistry of Meldrum's acid, the isopropylidene ester of malonic acid, which on pyrolysis fragmented to ketene, acetone, and carbon dioxide. Meldrum's acid readily condensed with aldehydes and ketones and the product of condensation of benzaldehyde when pyrolysed yielded benzylidene ketene, which could be isolated as its bright red dimer, and which at higher temperatures lost carbon monoxide and formed benzylidenecarbene, which finally rearranged to phenylacetylene.[5] The last reaction was shown to be reversible[6] and this simple method of making carbenes from acetylenes led to numerous studies.

The reversibility of this reaction raised the possibility of the triple bond in benzyne behaving the same way. The benzyne ring would be expected to contract with the formation of cyclopentadienylidenecarbene. This was the hypothesis used to plan a double labelling experiment and the experimental outcome was as predicted.[7] An alternative explanation was proposed by Curt Wentrup at the time, and the pathways put forward in 1984 are still being examined 30 years later.[8]

Further development of the research resulted, in 1979, in the formation of cyclopentadienylideneketene from Meldrum's acid derivatives and the loss of carbon monoxide from the ketene to yield cyclopentadienylidenecarbene and benzyne which brought these two approaches together.[9]

The work towards the original objective led, in the hands of Gabrielle McMullen, to methylene ketene[10] and the availability of this unstable compound opened up collaborative spectroscopic studies with those studying infrared spectroscopy, A. D. E. Pullin and M. J. Irvine,[9] and the group led by R. D. Brown and P. D. Godfrey studying microwave spectroscopy at Monash.[11] This research was pursued through extended cumulenones which were of interest principally for their spectroscopy.

Roger published 100 papers on pyrolysis and, to obtain an overview, it is perhaps best to read his last review,[12] written for a special issue of *Aust. J. Chem.* on benzyne chemistry. The wider field was reviewed on five occasions,[13] and his book covers the basic processes.[14]

Roger was always attracted to synthesis and his approach was always original, but his efforts in this field were less successful, although in some instances, the objective was achieved by later workers using the same strategy but different protective groups and milder reactions.[15] Each compound was chosen as an interesting exercise and all led to worthwhile teaching projects, but Roger, in his *Chemobiography*,[16] analyses his own limitations in this field and regrets the lack of continuity of the supply of doctoral students necessary for such exercises. An overview of his synthetic studies on natural products can be obtained from a series of papers,[17] but these do not include syntheses of heterocycles or studies on synthetic methods. He published 66 papers on subjects other than pyrolysis.

Roger made good use of study leave to learn new areas of chemistry. In 1966, the year after the first enunciation of the Woodward Hoffmann rules for orbital symmetry,[18] he collaborated with R. C. Cookson in Southampton on photochemistry and the outcome, a 1,3-shift of an allyl group without inversion,[19] was quoted by Woodward and Hoffmann in their book in 1970.[20] In 1971, Roger joined a former colleague, R. Bonnett, at Queen Mary College, London, to devise the first synthesis of isoindole using a pyrolysis reaction.[21] In 1978, he was in Oxford and Berkeley, but used his time to write his book.[14] But, again in 1985 with B. Zwanenburg at Nijmegen and in 1990 with H. MacNab in Edinburgh, Roger did experimental work in new areas of pyrolysis. Roger was never afraid to collaborate with other senior chemists and he took good care of his students and always acknowledged their contribution fully.

If we trace Roger's intellectual heritage through doctorates, we find A. R. Todd (1907–1997) obtaining his first Ph.D. with W. Borsche at Frankfurt am Main in 1931 and the second with R. Robinson at Oxford in 1933. Robinson (1886–1975) obtained his D.Sc. in 1910 with W. H. Perkin Junior (1860–1929), who completed his Ph.D. around 1883 with Adolph von Baeyer (1835–1917). Roger was the fifth in line in the 100-year European tradition stretching back to the first great expansion of organic chemistry, but from 1955 onwards, he also acquired a great deal from the American tradition, which has been so influential in the second half of the 20th century.

Roger was a very private person, very knowledgeable, well read, and abreast of current affairs. With Mary, he attended plays, concerts, operas etc. and, with an artist in the family, had to keep *au courant* with movements in art. He thought deeply about chemistry and has written that this was hard on his family, and on occasion it was detrimental to his health. For recreation, he spent time revegetating a bush block, later had a beach house and further occupied himself with silver smithing and building gossamer light model aeroplanes.

At Sydney University, Roger's whole way of thinking had to turn upside down as he learnt science. Similarly through his doctoral and post-doctoral studies, totally new ways of thinking had to be acquired. Numerous aspects of spectroscopy had to be understood as they were revealed over the years, and how many new theories and new ways of thinking in organic chemistry have arisen in the last 60 years? The intellectual ground on which we stand is always shifting and just as the modes of thought in the community in 2014 are totally different from what they were in 1954, so are the ways of thinking about chemistry. Roger's greatest wish always was that students would be original in their ideas and adventurous in their experiments. Let us hope the Journal benefits in the future from just such approaches.

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