

Roger F. C. Brown Memorial Issue

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The study of pyrolysis (thermolysis) reactions has a long tradition in Australia. In the 1950s, G. M. Badger and his students at the University of Adelaide carried out extensive studies on the gas-phase pyrolysis of aromatic hydrocarbons under flow conditions at atmospheric pressure.^[1] Experiments with low-pressure gas-phase pyrolysis, later to be known as flash vacuum thermolysis (FVT) or flash vacuum pyrolysis (FVP) – a term coined by Eddie Hedaya^[2] – were started by Wilfred D. (Bill) Crow and R. F. C. (Roger) Brown in the Chemistry Department, School of General Studies, at the ANU in 1965. At that time, there were two places in Canberra where one could do chemical research: the Medical Chemistry Department in the John Curtin School of Medical Research under Professor Adrien Albert, and the Chemistry Department in the School of General Studies. The Research School of Chemistry was being built in 1966 and it opened for business in 1967 with Arthur Birch as Foundation Dean. Nobody liked the name ‘School of General Studies’, which authors abbreviated SGS or dropped entirely in their publications, and in 1979 this unhappy name was changed to ‘The Faculties’.

Roger Brown arrived at the SGS as a young lecturer in 1961,^[3] and Bill Crow from CSIRO (Melbourne) accepted an associate professorship at about the same time. At the SGS, Bill Crow purchased a Lindberg tube furnace^[4] for his M.Sc. student from Western Australia, Richard K. (Dick) Solly to commence FVP experiments in 1964. He later purchased a mass spectrometer in order to pursue the then-popular line of research on analogies (or differences) between thermal and mass spectrometric fragmentations. Other researchers, inter alia M. P. Cava, E. K. Fields, and S. Meyerson in the USA had similar interests. However, Bill Crow went on study leave with Nelson J. Leonard at the University of Illinois, Urbana-Champaign, in 1965 and left it to Roger to supervise Dick, which led to a series of very topical papers on the formation of benzyne and hetarynes,^[5] a subject that remained close to Roger’s heart throughout his career. After his move to Monash University in 1968, methyleneketenes and methylenecarbenes became a major research topic in collaboration with Frank. W. Eastwood,^[3] and this is where the ‘Roger Brown rearrangement’, viz. 1,2-dyotropic shifts^[6] in acetylenes, $R-C\equiv C_2-R' \rightleftharpoons R'-C\equiv C_2-R$, taking place via transient vinylidene intermediates, was discovered.^[7] According to Richard Johnson (University of New Hampshire, USA), during the Gordon Conference on Physical Organic Chemistry in Holderness, New Hampshire, in 2001 he and Roger Brown discussed this chemistry as they hiked up Rattlesnake Mountain, and later that afternoon, Richard and Maitland Jones, Jr (Princeton University) decided (over a beer) to name the rearrangement after Roger. During the evening session, Maitland drew the alkyne-vinylidene rearrangement on a

chalkboard in the centre of the stage and suggested to the assembled crowd to honour Roger by naming the reaction after him.

The August issue of *Aust. J. Chem.* is dedicated to the memory of Roger Brown, who passed away on 1 September 2013. Many scientists from all over the world have contributed papers to this issue, which thereby becomes a celebration of FVP and the chemistry of reactive intermediates and unusual molecules as well as organic synthesis, structure determination, and inorganic chemistry. The apparatus and techniques used in flash (vacuum) pyrolysis are reviewed.^[4] Anna Chrostowska and Stanislaw Lesniak from Pau, France, and Lodz, Poland, respectively, review the use of photoelectron spectroscopy in the study of pyrolysis reactions.^[8] Ian Rae, Roger’s first Ph.D. student, reveals some of Roger’s first research projects at the SGS in Canberra, which were concerned with 1,2-dithiole chemistry and nitrones.^[9] Carl Th. Pedersen (Odense, Denmark) with colleagues in Belgium, Japan, and Singapore describe the elusive ethene diselone, $Se=C=C=Se$.^[10] Oliver Kappe (Graz, Austria) reports on the (non-)existence of special microwave effects,^[11] Hassan Sheibani (Kerman, Iran) on new reactions of chlorocarbonylketenes,^[12] and Wolfram Sander et al. (Bochum, Germany) on matrix-isolation of pyridyl radicals formed by FVP of azopyridines as well as the pyridylperoxy radicals derived from them.^[13] Arvid Kuhn and Curt Wentrup (UQ) with co-workers from Japan report on the characterisation of 1,2-dehydroheptafulvene (heptafulvyne) and rearrangements of C_8H_6 hydrocarbons under FVP conditions, which includes a Roger Brown rearrangement.^[14] Joel Hooper, J. W. White, and Andrew Holmes (Melbourne) describe the use of a Claisen rearrangement with an organocatalytic, intramolecular Diels-Alder reaction in natural product synthesis,^[15] Mary Garson et al. (UQ) report the isolation of a new 3-alkylpiperidine from Indonesian waters,^[16] and John Bremner and Z. Wu (Wollongong) detail annulation of eight- to ten-membered oxaza rings to benzo[*b*]thiophene.^[17] Chris Moody (Nottingham, UK) reports the use of Rh-catalyzed carbene insertion in the synthesis of indoxyl acid esters.^[18] Jonathan White, Ken Ghiggino and co-workers (Melbourne) elucidate solvatochromism in diketopyrrolopyrrole derivatives with the aid of calculations,^[19] Jason Smith (UTas), Rolf Prager (Flinders) and co-workers report on the synthesis of heterocyclic fused imidazoles by FVP of isoxazol-5(2*H*)-ones,^[20] and Ross McGeary (another former Roger Brown student) and his co-workers (UQ) use ethyl (benzothiazol-2-ylsulfonyl)acetate in malonic ester-type syntheses of carboxylic acids and esters.^[21] Roger Brown spent an extended period on sabbatical at Nijmegen University, The Netherlands, in Binne Zwaneburg’s group, and two papers from this laboratory report

on the preparative use of FVP in the synthesis of cyclopentenones.^[22,23] Craig Williams, Elizabeth Krenske and Paul Malek Mirzayans (UQ) detail a combined experimental and computational study of azomethine ylide formation from *N*-oxides.^[24] Glen Deacon, David Turner and co-workers (Monash) use high-temperature (solid state) chemistry to achieve an unexpected formation of a biquinolinolate ligand from 8-quinoline and rare-earth or transition metals,^[25] and Andrew Abell et al. (Adelaide) describe a preparation of macrocyclic calpain inhibitors.^[26] Steven Langford (Monash) reports on crown ether derivatised pyromellitic diimides,^[27] and David Black (UNSW, formerly of Monash) on the synthesis, structures, and conformations of bis-glyoxylamides derived from bis-acylisatin.^[28] Lawrence Scott (Boston College) and co-workers have investigated the mechanisms of aryl–aryl bond cleavages under FVP conditions,^[29] and R. Alan Aitken (St Andrews) describes the FVP of substituted benzo[*c*]thiopyran and thieno[2,3-*c*]thiopyran *S,S*-dioxides.^[30] Richard Johnson (New Hampshire) and his students invented ‘microwave flash pyrolysis’ and report here on its application in interconversion and dimerisation of C₉H₈ hydrocarbons (2-ethyltoluene, chrysene and others), including Roger Brown rearrangements.^[31] John Brown (Oxford) reports computational studies of the origin of stabilisation of bicyclo[3.2.1]octadienyl anion and related species,^[32] and Stephen Glover (Armidale) details studies of the structure, amidicity, and reactivity of *N*-chlorohydroxamic esters and *N*-chloro-β,β-dialkylhydrazides, which are anomeric amides with very low resonance energies, i.e. very low degree of the usual stabilisation of amides by delocalization.^[33] Bruce King and Henry F. Schaefer (University of Georgia) and their co-workers at South China Normal University report a computational study of the differences between mononuclear and binuclear manganese carbonyl cyanides and isoelectronic binary chromium carbonyls, which are attributed to the basicity of the cyanide nitrogen atom.^[34] Aaron Amick and Sara Martin (Washington College, Maryland) have discovered that an external radical source (hexane) greatly facilitates cyclodehydrogenation of polycyclic aromatic hydrocarbons (PAHs) under FVP conditions.^[35]

David Lupton and his co-workers (Monash) describe in a Communication that subjection of *N*-methyl carbazolone allyl carbonates bearing a propargyl side chain to Pd[0] catalysis leads to the formation of enantioenriched γ-lactones, rather than the expected products of decarboxylative allylation.^[36] Jia Cao and Patrick Perlmutter (Monash) report a facile, microwave-assisted, solvent-free synthesis of iodides from tosylates.^[37] Jean-Claude Guillemin and Gnon Baba (Rennes, France) describe the synthesis of highly unstable functionalized 1-alkynylarsines H₂C=CH–C≡C–AsH₂ and H–C≡C–C≡C–AsH₂.^[38]

Motivated by an interest in preparing thin polymer films by chemical vapour deposition, Ulfert Wiersum at Akzo-Nobel in Arnhem, The Netherlands, started investigations of pyrolysis reactions in 1972 and soon became a champion of preparative FVP. Later, he became interested in PAHs due to a need to understand soot formation in fluid catalytic cracking, and after retiring from Akzo-Nobel he synthesised commercial quantities of select PAHs in FVP reactions at home in his garage. Meanwhile, both Roger and I developed lasting friendships with Ulfert, and he collaborated with us both. It is fitting that Ulfert concludes this issue with a Focus article, ‘A Personal Note on the Development of Pyrolysis as a Synthetic and Mechanistic Technique in Organic Chemistry’.^[39]

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