Douglas Lloyd

A Tribute

It is a privilege to have been invited to write a tribute for this issue of ARKIVOC which is dedicated to Douglas.

Douglas Mathon Gent Lloyd, a westcountryman to his fingertips, studied chemistry at the University of Bristol under Wilson Baker. He graduated during World War II and went on to carry out research work on explosives for the Ministry of Supply at the University of Sheffield and, as a consequence, his first nine research publications are classified documents.

Immediately following his war service, he joined the academic staff of Department of Chemistry at the University of St Andrews where, even in his retirement, he remains an active and enthusiastic member. His early years in St Andrews clearly show how Douglas Lloyd's academic career would develop. Within a year of his appointment, he had published a research paper showing his life-long interest in furthering knowledge in science. Interestingly, both authors of this paper (Douglas Lloyd and John Read) which was published in the *Transactions of the Faraday Society* would today be regarded as organic chemists. In the following year, his laboratory manual, *Reactions of Simple Organic Compounds*, was published. In writing this he showed his enthusiasm for communicating chemistry to young people in lecture theatre, seminar room and laboratory. In addition, in his early years in St Andrews, he was warden of Deanscourt, a Hall of Residence for postgraduate students and academic visitors. Here he was able to offer friendship to many who were visiting this country for the first time.

When one of us (DRM) arrived in St Andrews in 1949, the Department of Chemistry consisted of Professor John Read and six academic staff. It was easy to get to know the academic staff and their interests and it was very clear that Douglas had interests, at that time, in alicyclic chemistry and non-benzenoid aromatics as well as in fine wines and cider. The long and
productive collaboration between DRM and DL started with an honours project on azulenes and continued, with DRM as one of Douglas' first PhD students, in a project involving an attempted synthesis of a diaza-azulene. The "final dehydrogenation" step did not, however, work due to the unexpected stability of the precursor 1. This observation resulted in the development of research into diazepine chemistry which has generated a series of 30 research papers, the early ones of which were published jointly with DRM and some of the later ones with Hamish McNab, also one of Douglas Lloyd's research students. Although 2,3-dihydro-1,4-diazepines 2 were already known, the work of Lloyd and Marshall, showing the retention of the delocalised –N=–C–C=–NH– system during bromination, was an early example of electrophilic substitution, now much more widely recognised, in quasi-aromatic systems.

![Diazepine structures](image)

Professor Roger Brown (formerly of Monash University, Australia) writes of this period:

“In 1956 I was a Ph.D. student in Cambridge with Sir Alexander Todd and Malcolm Clark, and we were thinking about approaches to B12/corrin synthesis when a paper by Lloyd and Marshall on the diazepines formed from 1,2-diamines and acetylacetone appeared in *J. Chem. Soc.* This was not a new class of compound, but Lloyd and Marshall found some interesting behaviour, notably preservation of the conjugated system on bromination, a kind of quasi-aromatic substitution. At that time non-aromatic heterocyclic chemistry was spread thinly through the literature, and the chemistry of simple conjugated systems of carbon and nitrogen was not well known. The importance of one such system emerged with the structure of Vitamin B12, which proved to be based on a ligand of highly simplified partial structure 3.

\[
\text{–N=–(C=–N=–C)2–C=–NH–} \quad \text{–N=–(C=–N=–C)}2\text{–CH–CH–NH}– \\
\]

3

Curiously, the first X-ray structure proposed for B12 was based on 4, in which conjugation is not complete. In terms of such stripped-down partial structures Lloyd and Marshall’s diazepines (and a later Cambridge half-corrin derived from pyrroline N-oxide chemistry) both have the same conjugated system –N=–C=–C–NH–.”

In the 1950s, the Lloyd group was quite small but as Douglas' interests expanded his group grew to include postdoctoral workers several of whom have continued with successful careers in
academic life. The chemistry of non-benzenoid aromatic compounds has always been at the core of much of Douglas' research. As well as the chemistry of diazepines he has made particularly significant contributions to ylide chemistry. This work began in the early 1950s (when the Wittig reaction was being developed elsewhere) with nitrogen ylides, such as pyridinium cyclopentadienide, and led on to the Lloyd group's interest in ylides involving other elements. This culminated in a series of landmark papers in the late 1960's (mostly with Mike Singer) reporting the isolation of the first ylides of antimony, bismuth, selenium and tellurium. These wider interests have often involved collaborative work within St Andrews and abroad taking his research into areas such as electrochemistry and X-ray and theoretical studies on molecular structure and bonding. Regular collaborators include Chris Glidewell (St. Andrews; theoretical), Ian Gosney (Edinburgh; ylides), Kalman Hideg (Pecs, Hungary; macrocycles), Hamish McNab (Edinburgh; diazepines), Donald Marshall (Bangor; diazepines) and Colin Vincent (St. Andrews; electrochemistry).

The breadth of his interests brought Douglas international recognition and he became a regular attender at Burgenstock meetings and at international symposia, being particularly associated with the ISNA series of meetings, the 5th of which was held in St Andrews in 1985 when he was the Local Arrangements Co-ordinator.

Roger Brown’s experiences are typical:
“I have had the pleasure of meeting Douglas on many occasions at conferences, especially ISNA symposia on Novel Aromatic Compounds. We have shared interesting experiences at table, from the complications of Japanese menus in Fukuoka to the grandeur of Afternoon Tea in the Empress Hotel, Victoria, B.C.”

His contributions to such meetings are, however, not entirely restricted to chemistry. A well established feature of RSC meetings held in St Andrews is the evening organ recital given by Douglas in St Salvator's College Chapel. The recitals, recently involving also Hamish McNab (flute), are always well received, not only because of his undoubted abilities as an organist but also because participants appreciate a performance by 'one of their own'. As well as the music, the participants are entertained by anecdotes about the chapel, the organ and the programme – but the highlight is invariably the performance of the rousing sortie composed by Monsieur Lefébure-Wély!

In addition to the many research articles and reviews, Douglas is the author of several books. Following on from his laboratory manual, came The Chemistry of Simple Organic Compounds and, some years later, A First Course in Organic Chemistry which have the same clarity and simple, lucid style as his undergraduate lectures. His four monographs on various topics in chemistry of alicyclic and conjugated cyclic compounds are written in the same highly readable style and include two authoritative monographs on non-benzenoid conjugated carbocyclic compounds (1966 and 1984). The latest major work which he has undertaken evolved through
his friendship with Wolf Walter at the University of Hamburg and used not only his wide knowledge of chemistry but also his knowledge of German. The translation of the 22nd Edition of *Beyer-Walter: Lehrbuch der Organischen Chemie* into English, has provided a comprehensive text and source book which contains in one volume much information which is invaluable to students and teachers alike but not found in standard English language text books of Organic Chemistry.

As a senior member of the academic staff of the University, Douglas Lloyd has been heavily involved in its affairs and it was no surprise when he was invited to be Provost of St Leonard's College when the college was re-established in 1973 as a postgraduate college of the University. Douglas did much through his Provostship to raise the profile of research within the University and provide a social environment for postgraduate students. Of much more benefit, however, to staff and students in Chemistry has been his willingness to listen and to offer help and advice when asked. The good ideas which have flowed from discussions with Douglas both formal and informal are innumerable.

Douglas has always been active in the affairs of the Royal Society of Chemistry and its predecessor bodies, the Chemical Society and the Royal Institute of Chemistry. In addition to his involvement with conferences, he has been involved in Local Section activities, Chemical Society Council, RSC Council and Perkin Council. In 1998 he became one of a select group who have published papers in learned journals over a 50 year period. He is a regular attender and active participant at Heterocyclic Group meetings. A Fellow of the Royal Society of Edinburgh, he regularly attends their meetings and has taken a special interest in their initiatives in promoting science to young people.

A keen traveller, especially by train and by ship on both of which he is a great authority, Douglas Lloyd has travelled widely – and he has the anecdotes to prove it! Although he and his wife, Lydia, will often relax by taking a cruise, many of his travels have been associated with chemistry. Particularly remembered are his periods as Visiting Lecturer at the University of Cape Town where his experience in undergraduate teaching was valued. These visits also provided Douglas with the opportunity to sample the Cape wines at a time when they were far less widely available in Britain and to sail to South Africa on the ships of the Union Castle Line.

Douglas and Lydia have welcomed a never ending flow of friends from home and abroad to their home in St Andrews where they have enjoyed fine hospitality both in food and in wine. If one could sum up Douglas Lloyd, the chemist, in one sentence, it would be: he spent much time giving lectures in universities and talking chemistry and drinking wine with his friends - a multifaceted, multilingual cosmopolitan.

December 2001
Publications of Douglas Lloyd

Research Papers

(1–9) Classified papers on nitro compounds, research on explosives for the Ministry of Supply, (1942–1945)


70. Diazepines. Part XV. Polarographic studies on six 2,3-dihydro-1,4-diazepinium perchlorates, Cleghorn, H. P.; Gaskin, J. E.; Lloyd, D. J. Chem. Soc. (B) 1971, 1615.


76. Reaction products from α,β-unsaturated ketones and aliphatic diamines or dithiols, Hideg, K.; Lloyd, D. J. Chem. Soc. (C) 1971, 3441.


78. Characteristics of the long wavelength spectral transitions and nuclear magnetic resonance studies of 1,4-diazepinium perchlorates, Cleghorn, H. P.; Gaskin, J. E.; Lloyd, D. Revista Latinoamericana de Quimica 1971, 103.

79. 5-Dimethylselenanyliden-2,2-dimethyl-4,6-dioxo-1,3-dioxan, ein neues stabiles selenoniumylid, Ernstbrunner, E.; Lloyd, D. Liebigs Ann. Chem. 1971, 753, 196.


101. Reaction of $\alpha,\beta$-unsaturated ketones with bis-nucleophilic reactants. Further studies with polyolefinic ($\alpha,\beta,\gamma,\delta$-unsaturated) ketones and $\beta$-heteroaryl (furyl and thietyl) $\alpha,\beta$-unsaturated ketones, Hankovszky, O. H.; Hideg, K.; Polgár, K.; Lloyd, D. Acta Chim. (Budapest) 1975, 85, 333.


162. A gentle method for the preparation of a variety of ylides (As, Sb, Bi, S, Te, thiouronium) from diazo compounds, Glidewell, C.; Lloyd, D.; Metcalfe, S. *Synthesis* 1988, 319.


164. Stibonium and bismuthonium ylides. A comparison with arsonium and other ylides, also including the crystal structure of triphenylarsonium bis(phenylsulphonyl)methylide and


181. Reviews and Book Chapters


### 203. Books

211. Lloyd, D. *The chemistry of conjugated cyclic compounds: To be or not to be like benzene?*; John Wiley and Sons; Chichester, 1989, pp 185.