

# Scientific genealogies of physical and mechanistic organic chemists<sup>1</sup>

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**Abstract:** Scientific genealogy trees of scientists who contributed to the study of organic reaction mechanisms over the last century are presented. The trees show doctoral and post-doctoral connections among scientists as well as connections between scientific ideas. Contributions made by scientists working in laboratories at Canadian universities and at the National Research Council of Canada are noted throughout. These trees, covering more than two centuries, are of interest to senior scientists and young students of science alike in understanding the evolution of scientific ideas and in career development for aspiring scientists. Key patterns revealed by these trees pertaining to ideas and discoveries made, how they were made, connections between them, and who made them are also discussed.

*Key words:* reaction mechanisms, physical organic chemistry, scientific genealogies.

**Résumé :** On présente les arbres généalogiques des scientifiques qui ont contribué à l'étude des mécanismes des réactions organiques au cours du dernier siècle. Les arbres mettent aussi en évidence les relations doctorales et postdoctorales ainsi que les corrélations entre idées scientifiques. Dans toute cette présentation, on met en relief toutes les contributions des scientifiques qui ont travaillé dans les laboratoires des universités canadiennes et ceux du Conseil national de recherches du Canada. Ces arbres, qui couvrent plus de deux siècles, présentent de l'intérêt autant pour les scientifiques bien établis que pour les jeunes étudiants des sciences en leur permettant de comprendre l'évolution des idées scientifiques et le développement des carrières des scientifiques ambitieux. On discute aussi des patrons clés révélés par ces arbres en relation avec les idées et les découvertes qui ont été faites, qui les a faites, comment elles ont été faites et des relations entre elles.

*Mots clés :* mécanismes réactionnels, chimie organique physique, généalogies de scientifiques.

[Traduit par la Rédaction]

## Introduction

In keeping with the theme of this special issue to emphasize the historical and current importance of mechanistic chemistry and the international impact that Canadian scientists have made to it, this paper presents scientific genealogy trees of prominent scientists who have made significant contributions to physical organic chemistry and reaction intermediate studies. Figure 1 shows a "super" tree with a timeline covering more than a century of scientific work that depicts key players as lynch pin nodes in the overall grand scheme of things. Detailed specific trees emanating from these people are available in the Supplementary material.<sup>2</sup> All of these trees were constructed using biographical information obtained from various sources: Poggendorff's Biographisches-literarisches Handwörterbuch zur Geschichte der exacten Naturwissenschaften (2nd ed., Wiley-VCH, Berlin), Biographical Memoirs of Fellows of the Royal Society (Vols. 1–50, The Royal Society, London), Obituary No-

tices of Fellows of the Royal Society (Vols. 1–9, The Royal Society, London), Biographical Memoirs of Fellows of the National Academy of Sciences of the United States of America (Vols. 1–84, National academy of Sciences, Washington, D.C.), Dictionary of Scientific Biography *Edited by* Charles C. Gillispie (Charles Scribner's Sons, New York), and various biographical references compiled in ref. 1. The following code applies to the trees: solid lines indicate doctoral advisor links, dashed lines indicate post-doctoral advisor links, boxes indicate people who brought knowledge from one country to another, and maple leaf icons indicate scientists who made contributions at Canadian universities and at the National Research Council of Canada. For each entry the name of the scientist is given along with the university where they did their doctoral work, the year of their Ph.D., and a chronological list of their notable contributions to the fields of physical organic chemistry and reaction intermediates. References to these contributions may be found in Tables S1, S2, S5, and S6 (Supplementary material) of

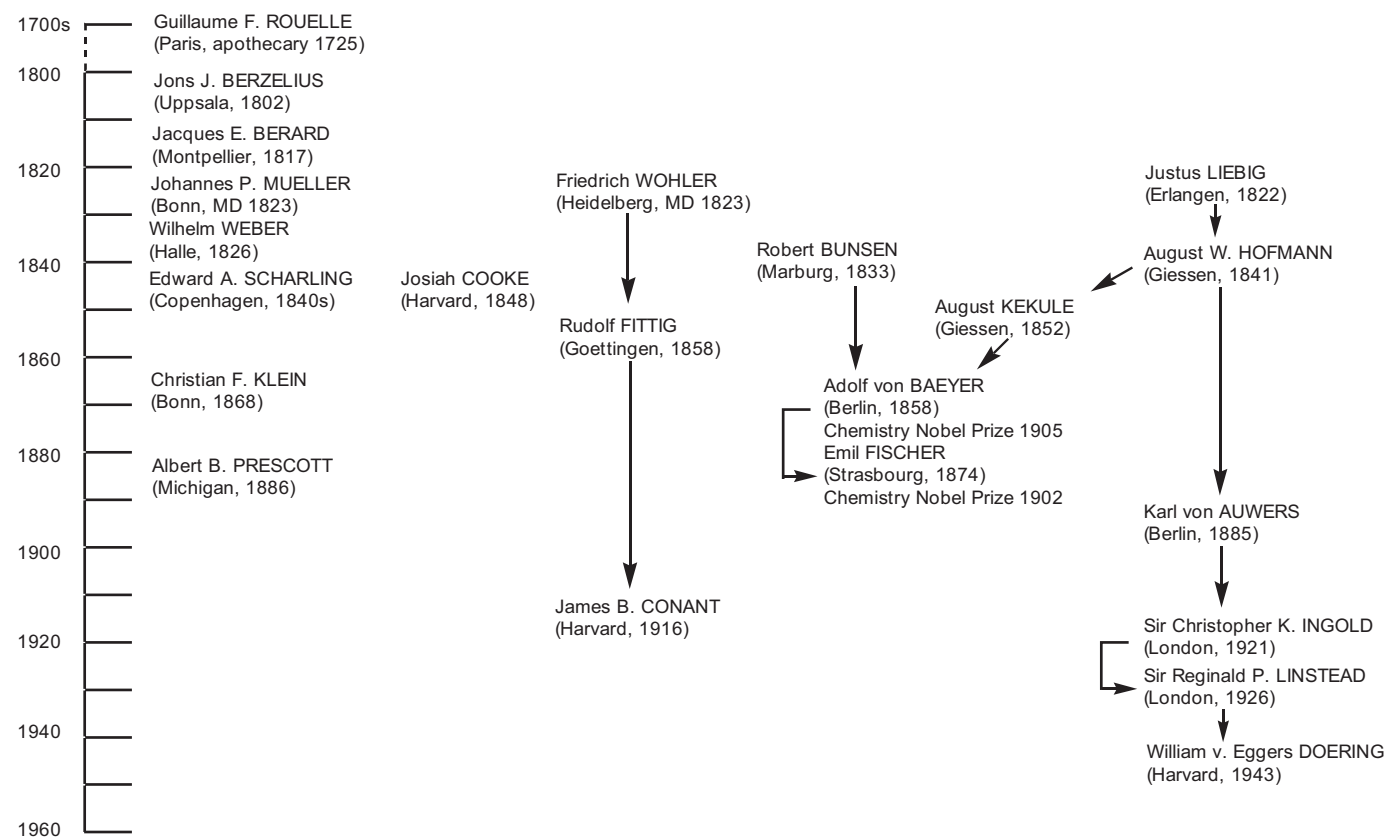
Received 10 May 2005. Published on the NRC Research Press Web site at <http://canjchem.nrc.ca> on 2 November 2005.

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<sup>1</sup>This article is part of a Special Issue dedicated to organic reaction mechanisms.

<sup>2</sup>Figures S1–S37 showing scientific genealogies of scientists contributing to organic reaction mechanisms and reaction intermediates. Canadian scientists are designated with a maple leaf icon. Supplementary data for this article are available on the Web site or may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0S2, Canada. DUD 4038. For more information on obtaining material refer to [http://cisti-icist.nrc-cnrc.gc.ca/irm/unpub\\_e.shtml](http://cisti-icist.nrc-cnrc.gc.ca/irm/unpub_e.shtml).

**Fig. 1.** Summary “super” scientific genealogy tree of key scientists whose scientific offspring contributed significantly to the development of mechanistic chemistry and to the discovery of reaction intermediates along with the timeline of the doctoral degree.



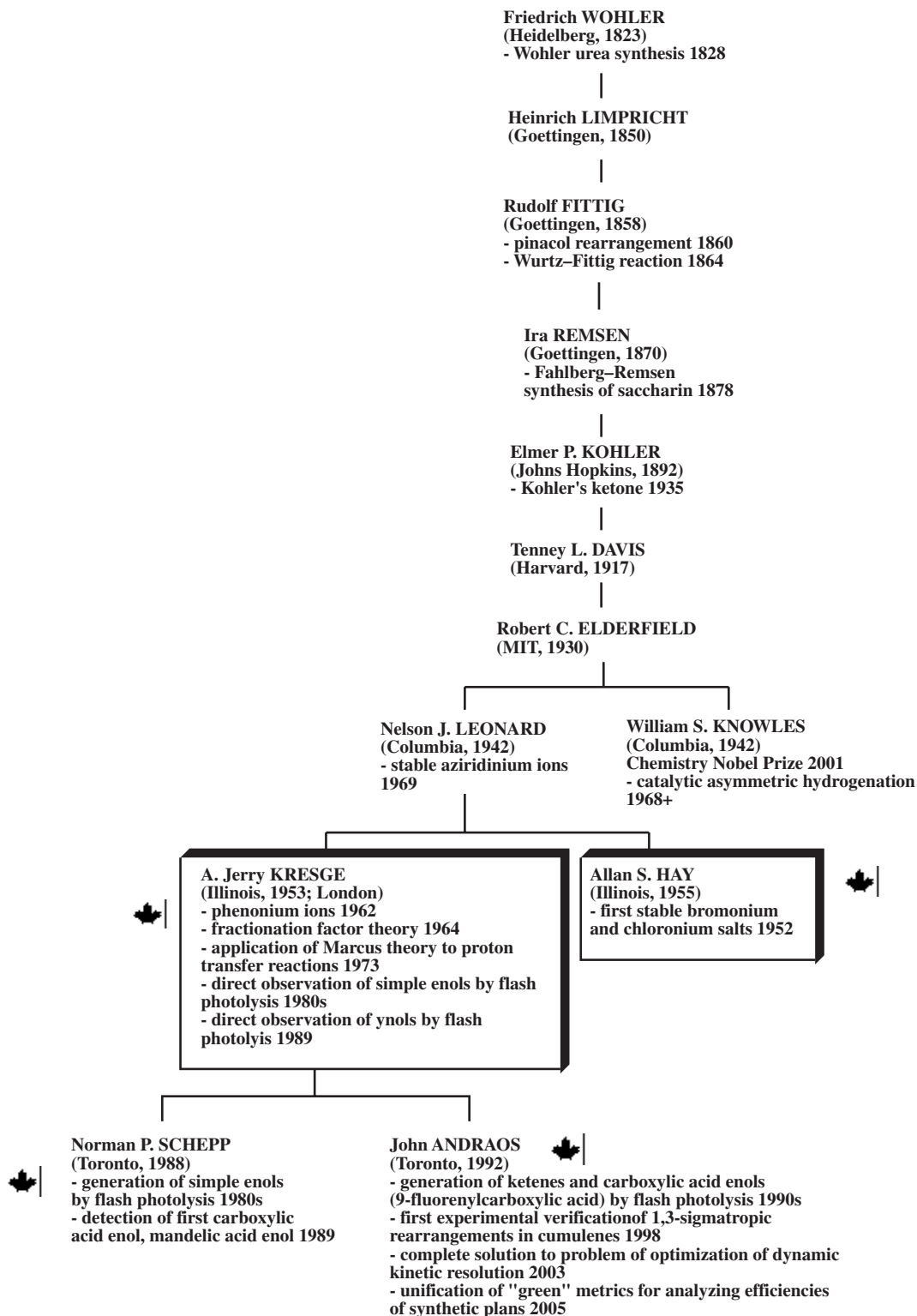
the following paper (2). These trees effectively trace how knowledge in physical organic chemistry emerged as a whole and how it came to Canada from the earliest times up to the year 2004. All professors of chemistry in Canada who made contributions to physical organic chemistry are included. In addition, particular attention was made to include in the compilation all Canadian contributors to this special issue. As an example, my personal scientific genealogy tree is shown in Fig. 2.

Though at first sight this compilation has obvious appeal to readers who may be interested only in the history of science, it is of far more fundamental and practical value with respect to conducting original research. From readings of biographical memoirs of famous scientists, one recognizes that nearly all of them can attribute their success in science in significant measure to their knowledge of how ideas progressed down the line from their forebears rather early in their careers in addition to the obvious traits of possessing intelligence, command of, and enthusiasm for their subject. Stamina, perseverance, and maintaining focus on key questions to be answered are particularly important virtues that academics require in the course of their work throughout their careers, especially when they are faced with convincing their peers of novel ideas that challenge established paradigms brought forward by scientists in positions of power and authority (3). One often can correctly guess that one must really have a good idea when one encounters stiff resistance to that idea. One is reminded of the following relevant statements made by a philosopher and physicist, respectively. “All truth passes through three stages before it is rec-

ognized. First, it is ridiculed. Second, it is violently opposed. Third, it is regarded as self-evident.” (Arthur Schopenhauer, 1788–1860) (4). “A new scientific truth does not triumph by convincing its opponents and making them see the light, but rather because its opponents eventually die, and a new generation grows up that is familiar with it.” (Max Planck, 1858–1947) (5).

Probably the most celebrated illustrations of these insights are the comments of Hermann Kolbe (1818–1884) on the imaginative ideas of Jacobus van’t Hoff (1852–1911, first recipient of the Nobel Prize in Chemistry in 1901) concerning the connection between the observation of optical activity in compounds and the presence of asymmetric carbon atoms in their molecular structures as exemplified by the following quotations. “...the weeds of a seemingly learned and brilliant but actually trivial and empty Philosophy of Nature, which, after having been replaced some fifty years ago by the exact sciences, is now once more dug up by pseudo-scientists from the lumber room of human fallacies, and like a trollop, newly attired in elegant dress and make-up, is smuggled into respectable company, to which she does not belong.” (6a). “Not long ago, I expressed the view that the lack of general education and of thorough training in chemistry was one of the causes of the deterioration of chemical research in Germany. Will anyone to whom my worries seem exaggerated please read, if he can, a recent memoir by a Herr van’t Hoff on *La Chimie dans l’Espace*, a document crammed to the hilt with outpourings of childish fantasy...This Dr. J.H. van’t Hoff, employed by the Veterinary Academy of Utrecht, has, so it seems, no taste for accurate

**Fig. 2.** Sample scientific genealogy tree showing doctoral advisor – student connections and flow of scientific ideas.



chemical research. He finds it more convenient to mount his Pegasus (evidently taken from the stables of the Veterinary Academy) and to announce how, on his bold flight to Mount Parnassus, he saw atoms arranged in space.” (6b).

A modern example documented in recent celebrations of the most cited papers in the *Journal of the American Chemical Society* in the last 125 years is that of Lineweaver and

Burk whose classic paper (7) is the most cited in that journal and yet at the time of review it was rejected several times by six reviewers, but the editor of the day took the risk and allowed publication (8). Now, of course, Lineweaver–Burk plots are routinely used in pharmacokinetic studies and are mentioned in virtually every undergraduate biochemistry textbook. Interestingly, the idea of plotting enzyme data in

this way came to them in their discussions when viewing data plots upsidedown as they were seated opposite each other at a desk! Another case is the postulation and discovery of the Koelsch radical in 1937 (9a), which was confirmed by ESR spectroscopy two decades later in 1957 (9b). This is actually an excellent example of how a new powerful technique helped to solve an old problem and thereby confirm prior indirect evidence of the existence of a chemical species.

Close examination of these genealogy trees reveals several important and revealing patterns that are relevant to the progression of the science itself and the career developments of the practitioners themselves. The following discussion is thus focused on two specific areas: the development of scientific discoveries in physical organic chemistry and reaction intermediates over time, and career development patterns among successful practitioners in the field. In the scientific development category we have: (1) leading chemists claiming discovery of the most number of reaction intermediates; (2) leading chemists claiming discovery of the most number of concepts in physical organic chemistry; (3) synthetic chemists who used principles and concepts in physical organic chemistry to advantage in organic synthesis; (4) physical and theoretical chemists who contributed to the development of physical organic chemistry concepts; and (5) highlights of achievements by Canadian chemists. In the career development category we have: (1) idea generation and connections, and distinguishing innovators from followers; and (2) leading academics in Canada who spawned the next generation of physical organic chemists in Canada. In the following compilation, leading scientists are listed in alphabetical order with their contributions. No ranking with respect to most important vs. least important discoveries is implied since all contributions are noteworthy and meritorious. Other scientists not given here who made contributions are noted in the genealogy trees (see Supplementary material).<sup>2</sup>

Leading chemists claiming discovery of the most reaction intermediates include:

- Paul D. Bartlett (bridged halonium ions (1936–1937), aziridinium ions (1947), and episulfonium ions (1949))
  - Keith U. Ingold (detection of phenyl radical (1953), benzyl radicals (1966), cumyloxy radicals (1969), peroxy radicals (1969),  $\beta$ -scission mechanism (1969), phosphinoyl radicals (1973), phosphinyl radicals (1973), and phosphinothionyl radicals (1973) by laser flash photolysis and electron spin resonance techniques)
  - George A. Olah (bridged halonium ions (1951), arenium ions (1956), dications (1966), phenonium ions (1969), and benzidine rearrangement dication (1972), all by generation in magic acid and detected by NMR spectroscopy)
  - Wilhelm Schlenk (stable carbanions (1910), ketyl radicals and radical anions (1911), metal radical anions (1914), the Schlenck–Brauns biradical or hydrocarbon (1915), and *p*-quinodimethanes (1919))
  - Julius Stieglitz (nitrenes (1896), carbocations (1899), tetrahedral intermediates (1899), and nitrenium ions (1913), all conjectured from comparative analysis of product structures with substrate structures)
  - Hermann Staudinger (ketenes (1905), *o*-quinonemethide (1911), and nitrenes (1917))
  - Saul Winstein (bridged halonium ions (1939), acetoxonium ions (1942), nonclassical norbornyl cation (1949), methoxonium ions (1952), phenonium ions (1952), and stable *p*-quinonemethides (1960))
- Leading physical organic chemists claiming introduction of the most number of named concepts in the field include:
- Louis P. Hammett (linear free energy relationships (1924), solvolysis reactions (1927), Hammett acidity function (1932), Hammett equation (1935), substituent effects and constants (1935), general acidity functions (1937), Zucker–Hammett hypothesis (1939), and Acree–Curtin–Hammett principle (1954))
  - Sir Christopher K. Ingold (concept of inductive effect (1923), concept of mesomeric or resonance effect (1924), concept of partial charges in chemical structures (1926), E1cb (1933), SN1 and SN2 (1934), E1 and E2 (1937–1948), and A1 and A2 (1941) mechanism categorizations, isotopic labelling experiment (1935), common ion effect (1940), normal salt effect (1940), principle of microscopic reversibility (1953–1969))
  - William P. Jencks (tetrahedral intermediates and catalysis in esterification reactions (1964), More O’Ferrall – Jencks diagram (1970), Jencks azide clock (1977), and Keefe–Jencks equations (1981))
  - C. Garner Swain (“push–pull” mechanism (1948), Swain–Scott equation (1953), Swain–Schaad equation (1958), and Swain–Lupton equation (1968))
  - Saul Winstein (anchimeric assistance or neighbouring group participation in solvolysis reactions (1939), normal salt effect (1940), Grunwald–Winstein equation (1948), intimate and solvent separated ion pairs (1952), special salt effects (1954), Winstein–Holness equation (1955), and concept of homoaromaticity and homoconjugation (1959))
- Leading synthetic chemists who have used mechanistic ideas to advantage in organic synthesis strategies include:
- Adolf von Baeyer (concept of angle strain (1885) and carbonium ion theory (1901))
  - Sir Derek H.R. Barton (the role of conformation in organic synthesis (1952))
  - Emil Fischer (lock and key model of enzyme catalysis (1894), experimental verification of tetrahedral asymmetry at carbon (1914))
  - Ernst O. Fischer (synthesis of transition-metal complexes of carbenes (1964), carbynes (1973), and ketenes (1983))
  - Moses Gomberg and Werner Bachmann (synthesis of *o*- and *p*-quinonemethides (1913) and synthesis of stable metal ketyl radicals and ketyl radical anions (1927))
  - Raymond U. Lemieux (Edward–Lemieux anomeric effect (1955–1969))
  - Hans Meerwein (Wagner–Meerwein rearrangement reaction (1922), synthesis of Meerwein oxonium salts (1937), and discovery of insertion of carbenes into C–H bonds (1942))
  - Sir Robert Robinson (curly arrow notation for reaction mechanisms depicting electron flow from electron donor sites to electron acceptor sites (1922–1932) and electronic theory of organic chemistry (1926))
  - Georg Wittig (Diels–Alder trapping of generated benzyne intermediate (1942), synthesis of *o*-quinodimethanes (1948), launched ylide chemistry (1948), and developed

the Wittig reaction and Wittig reagents to effect ketone-olefin transformations (1954))

- Robert B. Woodward (elucidation of structure of metallocene “sandwich” complexes (1952), concept of Woodward-Hoffmann rules to explain stereochemical product outcomes in thermal and photochemical electrocyclic reactions (1965))

Leading physical and theoretical chemists who made important contributions to mechanistic chemistry include:

- Henry Eyring (development of the absolute rate and transition state theory and Eyring equation (1935), electrode kinetics (1939), heterogeneous catalysis (1940), and solvent effects in kinetics (1940))
- Gerhard Herzberg (detection and spectroscopic identification of methyl radicals and singlet and triplet methylene (1956–1959))
- Gilbert N. Lewis (development of concepts of covalent bonding (1916), octet rule (1916), electrophilicity and nucleophilicity (1921), Lewis acidity and basicity (1923), and inductive effect (1923), advanced the idea that radicals and other paramagnetic species could be studied by magnetic methods (1923), investigated the effect of resonance on electronic transitions (1939), and discovery of the triplet state of ketones (1944))
- Rudolph A. Marcus (development of the Rice-Ramsperger-Kassel-Marcus theory (1951) and development of concepts in electron transfer theory including the Marcus equation and prediction of the inverted region (1956))
- Ronald G.W. Norrish and Lord George Porter (discovery of the Norrish type I and type II reactions (1935), development of the flash photolysis technique (1949), detection of acetoxy radicals (1952), benzyl radicals (1957), and phenyl radicals (1968))
- Linus Pauling (concept of electronegativity and development of the Pauling scale (1932), investigation of aromatic sigma complexes (1935), concept of hybridization in bonding (1948), and development of the Corey-Pauling-Koltun (CPK) space-filling models (1959))
- Michael Polanyi (development of the Bell-Evans-Marcus-Hammond-Polanyi-Thornton-Leffler principle (1936))
- Edward Teller (Renner-Teller effect (1934), Teller-Redlich product rule (1935), Jahn-Teller effect (1936), and the concept of principle of least motion (1938))

Great Canadian contributors to mechanistic and reaction intermediates chemistry include:

- Ronald J. Gillespie (valence shell electron repulsion theory (1963) and use of magic or superacid media to detect carbocation intermediates (1968))
- Keith U. Ingold (detection of phenyl radical (1953), peroxy radicals (1969),  $\beta$ -scission mechanism (1969), phosphinoyl radicals (1973), phosphinyl radicals (1973), and phosphinothionyl radicals (1973) by laser flash photolysis and electron spin resonance techniques)
- A. Jerry Kresge (fractionation factor theory applied to solvent isotope effects (1964), application of Marcus electron

transfer theory to proton transfer reactions (1973), and direct observations of enol (1980s), ynol (1989), ketene (1990s), and quinomethide intermediates by flash photolysis (2000s))

- Keith J. Laidler (application of theory of absolute reaction rates to problems in heterogeneous catalysis (1940), electrode kinetics (1939), and solvent effects in kinetics (1940), investigation of kinetics of the urea-urease system (1949), thermal free-radical reactions (1951), investigation of pH effects on enzyme kinetics (1955), and investigation of temperature effects on enzyme kinetics (1979))
- Frederick P. Lossing (detection of phenyl radical (1953), *p*-quinodimethanes (1955), and acetoxy radical (1955) by mass spectrometry, and investigation of free radicals in the gas phase by mass spectrometry (1957))
- Rudolph A. Marcus<sup>3</sup> (development of the Rice-Ramsperger-Kassel-Marcus theory (1951) and development of concepts in electron transfer theory including the Marcus equation and prediction of the inverted region (1956))
- E.W.R. Steacie (detection of benzyl radical (1954) and acetoxy radical (1955))
- Thomas T. Tidwell (synthesis of persistent bis(trimethylsilyl)ketenes (1992), synthesis of persistent allenylketenes (1997), synthesis of persistent silylketenes (1999))
- J.C. Tito Scaiano (development of the probe technique for detecting spectroscopically “invisible” transients (1977), development of time-resolved microwave dielectric absorption spectroscopy (1982, with Professor Richard Fessenden), development of the two-laser two-colour laser flash photolysis experiment for detecting excited state species tandemly generated from short-lived ground state transients (1984), trapping of carbenes to yield ylides such as pyridine ylide and thiocarbonyl ylides (1986), detection of ketene zwitterions by flash photolysis (1992), and development of the laser drop experiment for studying multiphoton excitation of photoprecursors (1993))

Successful academics invariably obtained their doctoral degrees and post-doctoral apprenticeships with scientists who were contemporary leaders in their fields. Horizontal comparisons across a contemporary generation in any tree reveal which ideas and discoveries were brought forward at nearly the same time. These also reveal people who may have been fellow colleagues, graduate students, or post-doctoral fellows at the bench in the same laboratory. A common trend is for people to do their post-doctoral training with the doctoral advisor of their own doctoral advisor, in effect their scientific “grandfather”. This pattern is particularly effective in securing consistent and credible recommendation letters from people who know one another professionally as well as personally. The German term *doktorvater* (doctor father) best describes a successful intellectual relationship between student and advisor. The following quotation from the Acknowledgements page of the 1933 M.Sc. thesis of Carl A. Winkler describing his relationship with his advisor Otto Maass is particularly pertinent. “In the brief space of two years since this work was begun, under

<sup>3</sup>Rudolph A. Marcus is included among the Canadians since he was born and raised in Montreal, Quebec and did his graduate work under Professor Carl Winkler at McGill University in 1946 and then became a post-doctoral fellow at NRC in Ottawa under E.W.R. Steacie. His theoretical training and later accomplishments in the study of electron transfer reactions came about from his association with Professor Oscar K. Rice at the University of North Carolina, who allowed him the freedom to pursue his ideas and publish on his own.

the direction of Dr. O. Maass, the writer has become aware of having worked not under, but with him. His generous assistance, invaluable and kindly criticisms, and unbound optimism, are emphasized by all those who have privileged to work with him. The interest which Dr. Maass evinces in the individual as a chemist is paralleled by his interest in the chemist as an individual. The author feels that to have worked with Dr. Maass is to have experienced the utmost in satisfactory relationships between student and director.” (10).

From the trees presented here one can readily deduce how personal relationships among scientists through advisor–student connections explain alliances with respect to collaborations or even rivalries and personal conflicts. In practical terms, it readily explains success in obtaining academic positions and academic job placement in particular institutions. Not surprisingly from the above quote, nearly 50 professors of chemistry across Canada, including Rudolf Marcus (1992 Nobel Chemistry Laureate), can trace their scientific genealogies directly to the Maass–Winkler combination, a statistical legacy that will likely remain unbroken. All of this information is hidden in the scientific literature and may not be so readily revealed, whether intentionally or unintentionally, particularly to new entering students in the field who may have the drive and intelligence to make the commitment to research, but require career guidance to channel their efforts in the right direction. The demands of fulfilling degree requirements and maintaining focus on the research problems at hand pose additional challenges to maintain the “big picture” outlook. Networking at conferences and talking with people at colloquia and other gatherings is the best way to penetrate this important area of knowledge as it is essential for successful career development.

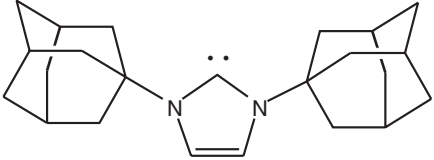
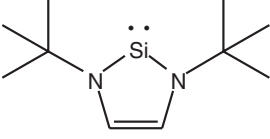
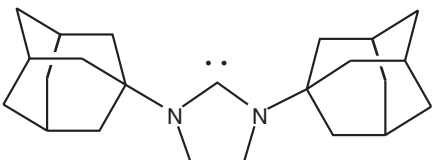
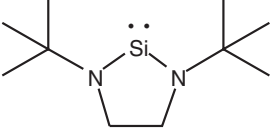
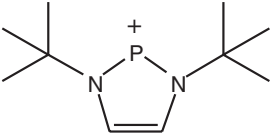
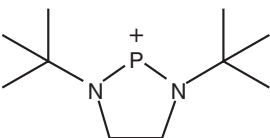
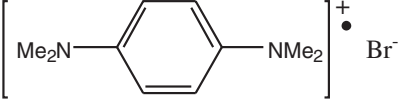
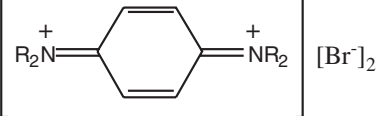
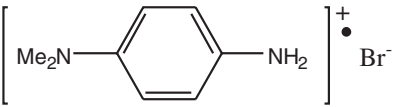
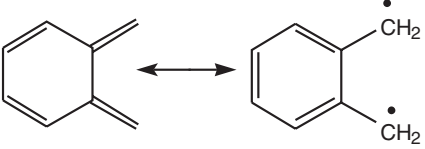
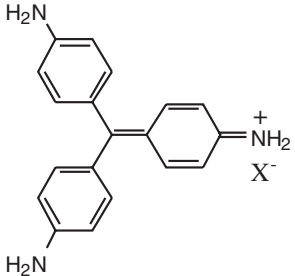
Another important spin-off of such genealogy trees is that predictability of what is important and worth looking into as a viable research question or area markedly improves when one knows the chronology of ideas and associates themselves with the key players in shaping those ideas or at least their direct scientific descendants. Naturally, as one would expect, the likelihood of making the “right connections” between various research areas increases as the size of the entire knowledge database grows. However, serendipity in the form of unexpected occurrences and chance “mistakes” always plays a strong hand and one must be prepared to recognize opportunities and act on them where possible. The most profound and dramatic connections often turn out to be those made between, at first sight, seemingly disparate fields. Nevertheless, despite the complexity of the maze, one is able to discern a certain logic in the ideas discovered over time, so that rather than them being presented or learned as a loose collection of dry facts, the trees serve to organize them into a meaningful whole. The big payoff is that student interest in the subject is enhanced and memory retention of information increases. A great motivation is the tantalizing prospect that if successful in significantly advancing the field, an aspiring student may one day join this growing “tree of knowledge”. What is important is knowing the connections between ideas and the context and circumstances in which those discoveries were made, ascertaining the limitations and levels of approximation employed, performing full

graphical critical point and dimensional analyses of key equations, and representing ideas using visualization techniques if possible. All of these can be best achieved by reading the published works of the originators of the discoveries themselves rather than relying solely on a textbook author’s “hand-me-down” interpretation of them. Peter Dervan’s following quote exemplifies the value of doing just that and how teaching can influence research. “During my first years at Cal Tech, I experienced how profoundly classroom teaching would influence my research. I taught Advanced Organic Chemistry, a reaction mechanisms course for graduate students. I never had the time to read in detail the original seminal papers of Winstein, Doering, Roberts, Olah and other pioneers of the field. Upon reading those key papers published mostly in the 1950s, I realized that these researchers set the stage for several decades of new inquiry in the field of reactive intermediates. My research should not be closing problems but rather opening new areas. I decided to choose a research problem that seemed hopeless in terms of current understanding, but would be suitable for thirty years of scientific inquiry.” (11).

Those researchers who follow this track early in their career paths are able to ask more penetrating questions and to chart new directions with greater confidence and thereby do worthwhile research of high quality. Knowing what is important and what is not is one of the key skills in charting a research agenda. In short, being able to see the big picture is imperative for success. Hence, the impact on one’s research plans is tremendous. In this vain, distinguishing innovators from followers becomes important. The reader may peruse these trees at leisure and consult them over several times and new ideas and revelations will surface. The reader is invited to explore these trees in a self-discovery approach and verify for themselves the previous points through their own personal experiences.

Table 1 lists some examples in the field of reaction intermediates of important idea and discovery connections between innovators and followers who themselves, in many cases, became innovators in their own right. Perusal of this list, particularly the structural similarities between juxtaposed reaction intermediates, illustrates and emphasizes points made in the preceding paragraph. Not surprisingly, therefore, students who have trained with any of the key scientific contributors or their immediate descendants are highly sought after as the next generation of academics. The thinking here is that their mentors’ successes will likely rub off on them as they chart their own research agendas, particularly if their doktorvater relationship had been positive. In fact, the most effective way for a scientist’s work to live beyond their time is for them to populate the next generation of academics with people that they have mentored, otherwise their names and work will inevitably be driven to extinction. This virtually guarantees that their ideas, contributions, and views will continue to influence scientific thought. Moreover, this strategy has a pay off for the advisor in the form of a “boomerang effect” with respect to fame, personal ego, the acquisition of prizes and research funds to continue their scientific work, and a growing publication list. However, this boomerang effect works in one direction; that is, if an advisor’s students are sought after it implies that the above benefits follow, but the converse may not always be true

**Table 1.** Idea and discovery connections between key players in physical organic and reaction intermediate chemistry through doctoral and post-doctoral scientific lineages.

| Innovating idea or discovery   | Following idea or discovery  |
|--|--|
| A.J. Arduengo, III: synthesis of stable imidazolylidenes and imidazolinyliidenes (Arduengo carbenes) (1991)              | M.K. Denk: synthesis of stable silylene analogues of Arduengo and Wanzlich carbenes (1994), phosphonium ions (1999)                              |
|   |    |
|   |    |
|  |    |
|  |   |
| A. von Baeyer: radical cations in the study of Wurster salts (1875) and synthesis of triphenylmethane dyes (1901 - 1905) | R. Willstätter: radical cations in the study of extended p-quinoid structures of p-phenylenediamine (1908) and study of o-quinodimethanes (1907) |
|                                       |    |
| Wurster's blue   |  |
|                                       |    |
| Wurster's red  |  |
|                                       |  |

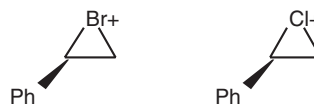
**Table 1** (continued).

A. von Baeyer: concept of angle strain in ring systems (1885)

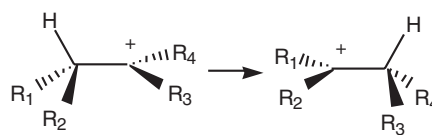
P.D. Bartlett: bridged bromonium and chloronium ions in the bromination and chlorination of styrene (1936 - 1937); aziridinium ions (1947); episulfonium ions (1949)

H. Sachse: Mohr-Sachse boat and chair conformations of cyclohexane (1890)

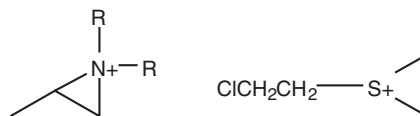
D.S. Tarbell: bridged bromonium and chloronium ions in the bromination and chlorination of styrene (1936 - 1937)



F.E. Condon and A. Schneider: Bartlett-Condon-Schneider reaction involving 1,2-proton shifts in carbocation intermediates (1944)

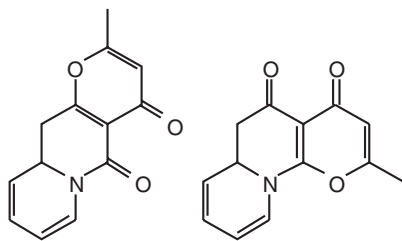


C.G. Swain: aziridinium ions (1947) and episulfonium ions in the solvolysis of mustards (1949)



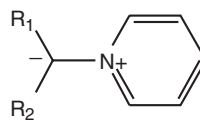
D.H.R. Barton: role of conformation in predicting product outcomes in organic synthesis (1952)

J. Berson: elucidation of the structure of pyridine adducts of ketene (1956)<sup>a</sup>



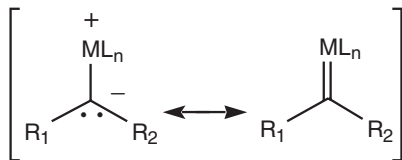
N. Holness: Winstein-Holness equation relating overall rate constant for appearance of product to relative populations of starting conformers (1955)

M.S. Platz: trapping of spectroscopically invisible carbenes with pyridine to yield coloured pyridine ylides in LFP experiments (1986)

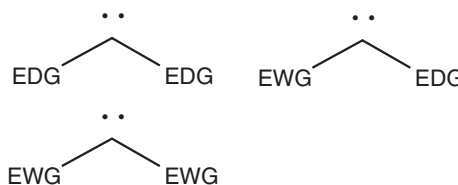


**Table 1** (continued).

G.L. Closs: discovery of carbenoids in cyclopropanation of olefins (1964); first absolute rate constant measurement of carbene reaction by LFP (1976)



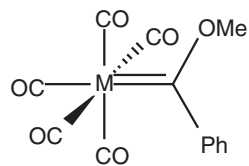
R.A. Moss: Hammett analysis of carbene and olefin reaction (1975); concept of philicity in singlet carbenes (1977)



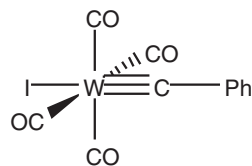
H. Eyring: development of the absolute rate and transition state theory and Eyring equation (1935), application of the absolute rate theory to electrode kinetics (1939), heterogeneous catalysis (1940)

K.J. Laidler: application of the absolute rate theory to electrode kinetics (1939), heterogeneous catalysis (1940), solvent effects in kinetics (1940), investigation of kinetics of the urea-urease system (1949), thermal free radical reactions (1951), investigation of pH effects on enzyme kinetics (1955), temperature effects on enzyme kinetics (1979)

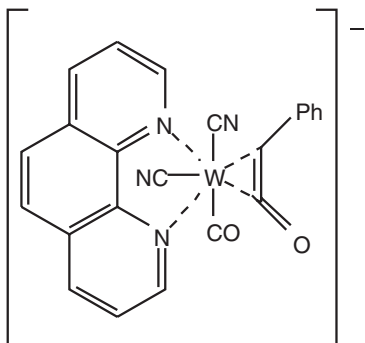
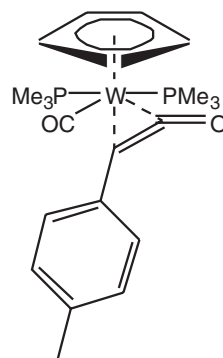
Ernst O. Fischer: synthesis of transition metal complexes of carbenes (1964), carbynes (1973), and ketenes (1983)



M = W, Cr, Mo



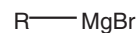
F. Kreissl: synthesis of transition metal complexes of ketenes (1976)



$[\text{Ph}_3\text{P}-\text{N}=\text{PPh}_3]^+$

Table 1 (continued).

V. Grignard: organometallic compounds and Grignard organomagnesium reagents for carbon-carbon bond forming reactions (1900)



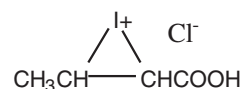
L.P. Hammett: concept of linear free energy relationships (1924) and Hammett equation (1935)

$$\log\left(\frac{K_X}{K_H}\right) = \rho\sigma \quad (\text{for equilibrium reactions})$$

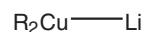
$\log\left(\frac{k_X}{k_H}\right) = \rho\sigma$  (for irreversible reactions)

where  $\sigma$  is the substituent constant and  $\rho$  is the reaction constant

C.K. Ingold: bridged halonium ions in the reaction of 2-butenoic acid with ICl (1931)



H. Gilman: Gilman organocuprate reagents for carbon-carbon bond forming reactions (1936)

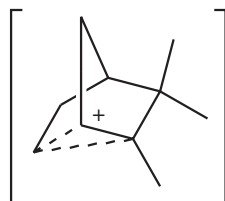


R.W. Taft Jr.: Taft equation (1952)

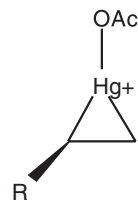
$$\log\left(\frac{k_X}{k_H}\right) = \rho^*\sigma^* - SE_S$$

where  $\sigma^*$  is the substituent polar effect constant,  $E_S$  is the substituent steric effect constant, and  $\rho^*$  and  $S$  are the corresponding reaction constants

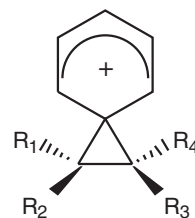
C.L. Wilson: suggestion of bridged carbocations as intermediates in the Wagner–Meerwein rearrangement of camphoryl chloride (1939)



A.G. Brook: bridged mercurinium ions in the oxymercuration of olefins (1950)

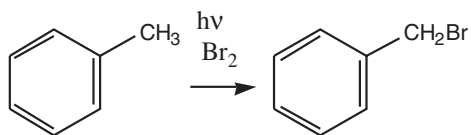
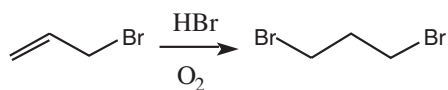
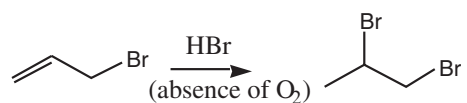


D.J. Cram (1949), S. Winstein (1952), A.J. Kresge (1962): study of phenonium ions

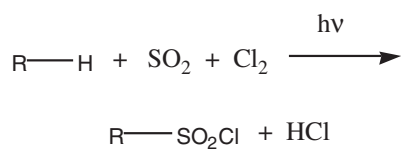
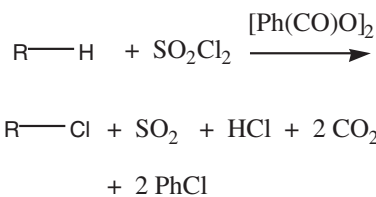
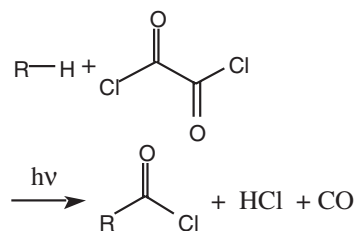
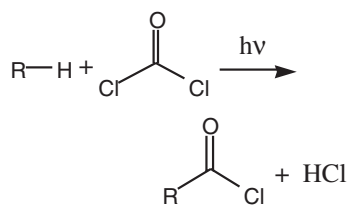


**Table 1** (continued).

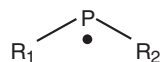
M.S. Kharash: study of radicals in solution phase reactions (1930s)



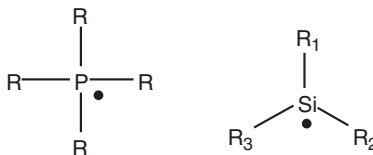
H.C. Brown: study of radicals in chloroformylation and chlorosulfonation reactions (1940)



W.H. Urry: phosphinyl radicals (1945)

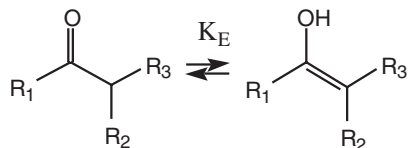


C. Walling: phosphoranyl radicals (1959) and silyl radicals (1966)



**Table 1** (continued).

A.J. Kresge: detection and measurement of keto-enol equilibrium constants for simple ketones in aqueous solution (e.g., acetone) (1984)

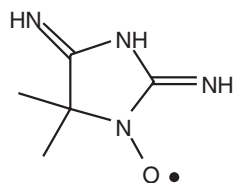


G.N. Lewis: concept of covalent bonding (1916)

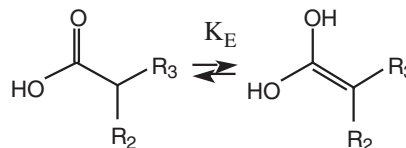
J.U. Nef: concept of tautomerism (1877)

R.G.W. Norrish: discovery of the Norrish Type I and Type II photoreactions (1935); development of flash photolysis technique (1949)

O. Piloty: synthesis of the first organic nitroxide, porphyrine (1901)



N.P. Schepp: detection and measurement of keto-enol equilibrium constants for enols of carboxylic acids in aqueous solution (mandelic acid) (1989)



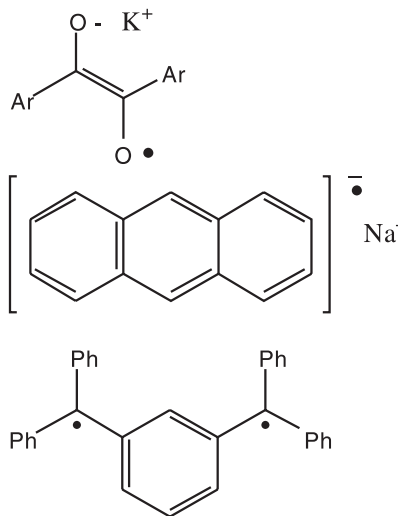
W.M. Latimer and W.H. Rodebush: concept of hydrogen bonding (1920)

S.F. Acree: proposed Acree-Curtin-Hammett principle based on product studies of diazomethanation of various tautomeric forms of phenylurazoles (1907)

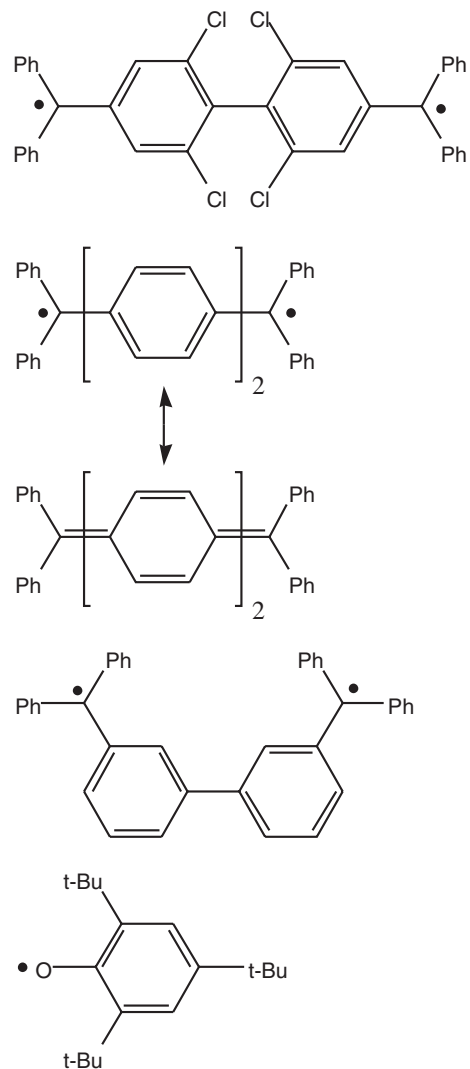
G. Porter: development of flash photolysis technique (1949)

J. Wirz: detection of ynoyl intermediate by laser flash photolysis (1989)

W. Schlenk: synthesis of stable ketyl radicals (1911), metal radical anions (1914), and the Schlenk-Brauns hydrocarbon (biradical) (1915)



E.F.W. Müller: synthesis of Müller's hydrocarbon (biradical) (1935), Müller-Müller-Rodloff biradical rule (1935); magnetic susceptibility measurements on ketyl radicals and ketyl radical anions (1936); discovery of 2,4,6-tri-*t*-butylphenoxy radical (1955)

**Table 1** (continued).

S.P.L. Sorensen: development of pH scale (1909)

J.K.W.F. Tiemann: first proposal of nitrenes as intermediates in the Lossen rearrangement (1891)

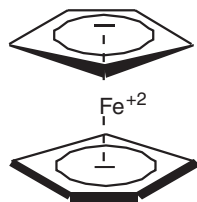
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J.N. Brønsted: development of acidity concept (1923), catalysis law (1924 - 1928)

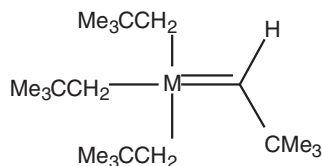
J. Stieglitz: suggestion of nitrenes as intermediates (1896)  
 H. Staudinger: nitrenes (1917)

**Table 1** (concluded).

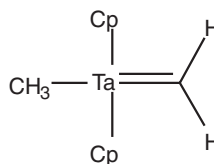
G. Wilkinson: elucidation of the structure of ferrocene (1952)



R.R. Schrock: synthesis of tantalum and niobium carbene complexes (Schrock carbenes) (1974)



M = Ta, Nb



**Note:** See Tables S1, S5, and S6 in the Supplementary material in the following paper (2) for the original references.  
<sup>a</sup>J.A. Berson and W.M. Jones. *J. Am. Chem. Soc.* **78**, 1625 (1956).

depending on how generous or selfish an advisor is in letting their students pursue their own ideas and allow them to shine. This leads to the key question a research student should ask of their prospective advisor before ranking them according to their area of research, prizes, their publication list, and other recognition measures: “What were the career fates of past students and research fellows who passed through that research group?”. Sydney Brenner (2002 Physiology and Medicine Nobel Laureate) offers the following succinct insight in his autobiographical sketch on the point of reprioritization of selection criteria of advisors for students when choosing their potential research mentors (12): “I believe that a scientist should be judged by the quality of the people he has helped to produce and not by prizes or other honours bestowed on him.”

These positive influences are tempered by the fact that the achievements of a research advisor are linked directly to the successes of their students. Simply put, an advisor is only as good as his or her students. Also, another tempering point is that there is an expectation and promise that these budding scientists make notable future discoveries and expand fundamental knowledge over their own careers. In this vein, faculty members in Canada who have been most successful in placing their students and post-doctoral fellows in academic positions in departments of chemistry in Canada in the fields of pure and applied physical organic chemistry and related areas are given in the following. University names in parentheses denote where these people have worked or are currently charting their careers.

Ronald J. Gillespie:

Felix Aubke (University of British Columbia)  
 Thomas Birchall (McMaster University)  
 Howard J. Clase (Memorial University)  
 Philip A.W. Dean (University of Western Ontario)  
 John S. Hartman (Brock University)  
 John B. Milne (University of Ottawa)  
 Jack Passmore (University of New Brunswick)

J. Wilson Quail (University of Saskatchewan)  
 Edward A. Robinson (University of Toronto)  
 Gary J. Schrobilgen (McMaster University)  
 John B. Senior (University of Saskatchewan)  
 Robert C. Thompson (University of British Columbia)  
 William A. Whitla (Mount Allison University)  
 J.C. Tito Scaiano:  
 Pamela A. Arnold (University of Ottawa)  
 Jeffrey T. Banks (Acadia University, University of New Brunswick)  
 Monica Barra (University of Waterloo)  
 Cornelia Bohne (University of Victoria)  
 Gonzalo Cosa (McGill University)  
 Frances L. Cozens (Dalhousie University)  
 Christopher Evans (Ryerson University)  
 William J. Leigh (McMaster University)  
 Matthew J. Lukeman (Acadia University)  
 William Skene (Université de Montréal)  
 Keith Yates:  
 Robin A. Cox (University of Toronto)  
 Alan C. Hopkinson (York University)  
 Robert A. McClelland (University of Toronto)  
 Robert S.B. McDonald (Mt. Saint Vincent University)  
 Paul G. Mezey (University of Saskatchewan, Memorial University)  
 James A. Pincock (Dalhousie University)  
 Oswald S. Tee (Concordia University)  
 Peter Wan (University of Victoria)  
 Keith U. Ingold:  
 Jeffrey T. Banks (Acadia University, University of New Brunswick)  
 Philip J. Dutton (University of Windsor)  
 Linda J. Johnston (NRC, Ottawa)  
 Janusz Lusztyk (NRC, Ottawa)  
 J.C. Tito Scaiano (NRC, University of Ottawa)  
 Danial D.M. Wayner (NRC, Ottawa)  
 Russell J. Boyd:

- Axel D. Becke (McMaster University)  
 Natalie M. Cann (Queen's University)  
 Katherine V. Darvesh (Mt. Saint Vincent University)  
 James W. Gauld (University of Windsor)  
 Brian A. Pettitt (University of Winnipeg)  
 Stacey D. Wetmore (Mount Allison University)  
 Ross E. Robertson:  
 James B. Hyne (University of Calgary)  
 Kenneth T. Leffek (Dalhousie University)  
 Alan Queen (University of Manitoba)  
 John Marshall William Scott (Memorial University)  
 Allan R. Stein (Memorial University)  
 John Steve Hartman (Brock University)  
 E.W.R. Steacie:  
 James B. Farmer (University of British Columbia)  
 Hyman D. Gesser (University of Manitoba)  
 Harry E. Gunning (University of Alberta)  
 Douglas G. James (University of British Columbia)  
 John C. Polanyi (University of Toronto)  
 David C. Walker (University of British Columbia)  
 Imre G. Csizmadia:  
 John D. Goddard (University of Guelph)  
 Alan C. Hopkinson (York University)  
 Roy E. Kari (Laurentian University)  
 Paul G. Mezey (University of Saskatchewan, Memorial University)  
 Raymond A. Poirier (Memorial University)  
 Keith J. Laidler:  
 Harvey Kaplan (University of Ottawa)  
 Michael T.H. Liu (University of Prince Edward Island)  
 Leon F. Loucks (University of Prince Edward Island)  
 Keith G. McCurdy (University of Lethbridge)  
 Donald J. McKenney (University of Windsor)  
 Ronald H. Kluger:  
 B. Jik Chin (University of Toronto)  
 Andrew S. Grant (Mount Allison University)  
 Scott D. Taylor (University of Toronto)  
 Gregory R.J. Thatcher (was at Queen's University)  
 John Paul Pezacki (NRC, Ottawa)  
 John Warkentin:  
 Robin A. Cox (University of Toronto)  
 Adrian L. Schwan (University of Guelph)  
 John Paul Pezacki (NRC, Ottawa)  
 Paul R. West (University of Victoria)  
 Saul Wolfe:  
 Howard Alper (University of Ottawa)  
 Glenn E. Palmer (University of Prince Edward Island)  
 Arvi Rauk (University of Calgary)  
 Donald F. Weaver (Dalhousie University)  
 Donald R. Arnold:  
 James A. Pincock (Dalhousie University)  
 William J. Leigh (McMaster University)  
 Danial D.M. Wayner (NRC, Ottawa)  
 Richard F.W. Bader:  
 Andre D. Bandrauk (Université de Sherbrooke)  
 Thanh T. Nguyen Dang (Laval University)  
 Kathleen M. Gough (University of Manitoba)  
 Adrian G. Brook:  
 Kim M. Baines (University of Western Ontario)  
 Gary J.D. Peddle (University of Alberta)  
 Cecil M. Warner (University of Guelph)  
 Erwin Buncel:  
 Helen A. Joly (Laurentian University)  
 Richard A. Manderville (University of Guelph)  
 David R.J. Palmer (University of Saskatchewan)  
 James T.C. Wojtyk (University of Prince Edward Island)  
 A. Jerry Kresge:  
 Andrew S. Grant (University of Winnipeg, Mount Allison University)  
 Norman P. Schepp (Dalhousie University)  
 Robert A. McClelland:  
 Judy L. Bolton (was at Queen's University, now at University of Illinois at Chicago)  
 R. Bruce Lennox (McGill University)  
 Frances L. Cozens (Dalhousie University)  
 Thomas T. Tidwell:  
 Richard F. Langler (Mount Allison University)  
 Daryoush Tahmessebi (St. Francis Xavier University, Brandon University)

## Acknowledgements

Parts of this work were presented at the 29th Ontario–Quebec Physical Organic Chemistry Mini-Symposium, 2–4 November, 2001, York University, Toronto, Ontario.

Though best efforts were made in this work to recognize as many key contributors to the study of reaction intermediates as far as possible, any remaining errors and (or) omissions in any of the compilations is unintentional.

## References

1. J. Andraos. Named things in chemistry and physics [online]. Available from <http://www.careerchem.com/NAMED/Homepage.html> [accessed July 2004]. 2001.
2. J. Andraos. *Can. J. Chem.* **83**, 1415 (2005).
3. H.C. Brown and P.v.R. Schleyer. *The nonclassical ion problem*. Plenum Press, New York. 1977. pp. 8 to 9.
4. A. Schopenhauer. *On the wisdom of life: essays and aphorisms*. Translated by R.J. Hollingdale. Penguin, Middlesex. 1970.
5. M. Planck. *Scientific autobiography and other papers*. Translated by F. Gaynor. Philosophical Library, New York. 1949. pp. 33 to 34. See also: C.C. Gaither and A.E. Cavazos-Gaither. *Scientifically speaking: a dictionary of quotations*. Institute of Physics Publishing, Bristol. 2000. p. 348.
6. (a) A.W.H. Kolbe. *J. Prakt. Chem.* **14**[n.f.], 268 (1876); (b) A.W.H. Kolbe. *J. Prakt. Chem.* **15**[n.f.], 473 (1877). See also: M. Polanyi. *Personal knowledge: towards a post-critical philosophy*. The University of Chicago Press, Chicago. 1962. pp. 155 to 156.
7. H. Lineweaver and D. Burk. *J. Am. Chem. Soc.* **56**, 658 (1934).
8. R. Dagani. *Chem. Eng. News*, **81**, 26 (2003).
9. (a) C.F. Koelsch. *J. Am. Chem. Soc.* **54**, 4744 (1932); (b) C.F. Koelsch. *J. Am. Chem. Soc.* **79**, 4439 (1957).
10. C.A. Winkler. M.Sc. thesis, McGill University, Montreal, Quebec. 1933.
11. P. Dervan. *Bioorg. Med. Chem.* **9**, 2215 (2001).
12. T. Frängsmyr (*Editor*). *Les Prix Nobel. The Nobel Prizes 2002* [online]. Available from <http://www.nobelprize.org/medicine/laureates/2002/brenner-autobio.html> [accessed May 2005]. 2003.