Reaction Intermediates in Organic Chemistry: the "Big Picture"

John Andraos
Department of Chemistry, York University, Toronto, ON M3J 1P3
jandraos@yorku.ca
FAX: 416-736-5936

Supplementary Material

Table S1. List of important concepts in physical organic chemistry by year of discovery.[a]

Year	Concept in physical organic chemistry (scientists)[b]
1836	Berzelius-Ostwald catalysis concept
1850	laws of chemical kinetics (van't Hoff, J.H./Wilhelmy, L.F.)
1877	tautomerism (Laar, C./Butlerov, A./Baeyer, A./Wislicenus, J./Meyer, K.H./ Knorr, L./Nef, J.U./Michael, A.)
1883	catalysis (Ostwald, W.)
1884	Le Châtelier's principle
1887	ionization theory (Arrhenius, S.)
1889	Arrhenius equation
1890	chair and boat ring conformations (Sachse, H./Mohr, E.)
1890	existence of stereoisomers (Meyer, V./Auwers, K. von/Eiloart, A.)
1893	Walden inversion rule
1894	steric effect (Meyer, V.)
1899	reaction intermediates concept (carbocations and tetrahedral intermediates) (Stieglitz, J./Norris, J.F.)
1901	carbonium ion theory (von Baeyer, A./Kehrmann, F.)
1907	Curtin-Hammett principle (Acree, S.F. - originator of concept)
1910	directing groups in aromatic chemistry (Holleman, A.F.)
1910	Hill plot
1913	Bodenstein steady-state approximation
1913	**Michaelis-Menten equation**
1914	potential energy surfaces (Marcelin, R.)
1915	pH indicators (Lubs, H.A./Clark, W.M./Acree, S.F.)
1916	covalent bonding (Lewis, G.N.)
1916	octet rule (Lewis, G.N./Langmuir, I.)
1919	Nernst radical chain

1919 Stern-Volmer plot and kinetics
1920 hydrogen bonding (Latimer, W.H./Rodebush, W.H./Huggins, M.L.)
1921 electrophilicity-nucleophilicity (Fry, H.S./BrØnsted, J.N./Lowry, T.M./ Lapworth, A./Lewis, G.N.)
1923 Lewis acid
1923 inductive effect (Lewis, G.N./Ingold, C.K./Lowry, T.M.)
1923 BrØnsted catalysis law
1923 BrØnsted-Lowry acid
1923 connection between S_N2 mechanism and Walden inversion rule (Kenyon, J./Phillips, H.)
1923 Idea that radicals could be studied by magnetic methods (Lewis, G.N./Taylor, N.W.)
1924 linear free energy relationships (BrØnsted, J.N./Pedersen, K./Hammett, L.P.)
1924 mesomeric (resonance) effect (Lucas, H.J./Arndt, F./Ingold, C.K.)
1926 Guggenheim method
1926 electronic theory of organic chemistry (Robinson, R./Ingold, C.K.)
1926 curly arrow notation to describe electron flow in reaction mechanisms and directing groups in aromatic substitution reactions (Robinson, R.)
1926 concept of partial charges in chemical structures (Ingold, C.K.; Ingold, E.H.)
1927 Born-Oppenheimer approximation
1927 solvolysis (Ward, A.M./Hammett, L.P.)
1930 electrostatic (field) effect (London, F.)
1930 Mills-Nixon effect
1932 Hammett acidity function
1932 Pauling electronegativity scale
1932 Hanes-Woolf plot
1933 Bell equation
1933 peroxide effect (Kharasch, M.S./Mayo, F.R.)
1934 hyperconjugation (Wheland, G.W.)
1934 S_N1/S_N2 (Ingold, C.K./Hughes, E.D.)
1934 Lineweaver-Burk plot
1935 Baker-Nathan effect
1935 Eyring equation
1935 Hammett equation
1935 Eyring transition state theory
1935 substituent effect (Hammett, L.P.)
1935 isotopic exchange (Urey, H.C.)

1935 isotopic labelling experiment (Urey, H.C./Ingold, C.K./Rittenberg, D./ Schoenheimer, R.)
1935 concept of resonance hybrids (Bury, C.R.)
1935 Müller-Müller-Rodloff biradical rule
1936 Gross-Butler equation
1936 Bell-Evans-Polanyi principle
1936 isotope effect (Reitz, O.)
1937 crossover experiment (Hurd, C.D.)
1937 acidity function (Hammett, L.P.)
1937 concept of chain transfer and vinyl polymerization kinetics (Flory, P.J.)
1938 principle of least motion (Rice, F.O./Teller, E.)
1939 Zucker-Hammett hypothesis
1939 effect of resonance on electronic transitions (Pauling, L./Lewis, G.N./Calvin, M.)
1939 anchimeric assistance (Winstein, S.)
1939 electrode kinetics (Eyring, H./Laidler, K.J.)
1940 heterogeneous kinetics (Eyring, H./Laidler, K.J.)
1940 solvent effects in kinetics (Eyring, H./Laidler, K.J.)
1940 common ion effect (Ingold, C.K.)
1940 normal salt effect (Ingold, C.K./Winstein, S.)
1940 stopped flow technique (Chance, B./Gibson, Q.H.)
1941 A1 and A2 mechanisms (Ingold, C.K.)
1942 Wheland intermediate
1944 B-strain (bond) (Brown, H.C.)
1945 F-strain (force) (Brown, H.C.)
1945 Pitzer ring strain
1947 Bigeleisen-Wolfsberg equation
1948 Grunwald-Winstein equation
1948 hybridization in chemical bonding (Pauling, L.)
1948 E1/E2 eliminations (Ingold, C.K./Hughes, E.D.)
1948 "push-pull" mechanism (Swain, C.G.)
1949 time resolved spectroscopy and kinetics (Norrish, R.G.W./Porter, G./Eigen, M.)
1949 Scatchard plot
1949 enzyme kinetics of urea-urease system (Laidler, K.J.)
1950 I-strain (internal) (Brown, H.C.)
1952 Taft equation
1952 conformation in organic synthesis (Barton, D.H.R./Hassel, O.)

1952 intimate and solvent separated ion pairs (Cram, D.J./Winstein, S.)
1952 Perturbational Molecular Orbital (PMO) Method (Dewar, M.J.S.)
1953 Doering-Zeiss intermediate
1953 Leffler hypothesis
1953 Swain-Scott equation
1953 NMR lineshape analysis and coalescence phenomena (Gutowsky, H.S.)
1953 interpretation of pH rate profiles as straight line segments (Dixon, H.)
1954 Curtin-Hammett principle (see 1907)
1954 special salt effect (Winstein, S.)
1954 matrix isolation spectroscopy (Pimentel, G.)
1955 Hammond postulate
1955 Winstein-Holness equation
1956 Edwards equation
1956 Marcus equation
1956 King-Altman method
1957 Gillespie-Nyholm model
1957 Zimmerman-Traxler transition state
1958 Swain-Schaad equation
1958 Kosower Z-values
1959 Corey-Pauling-Koltun space filling models
1959 temperature jump technique (Eigen, M.)
1959 Karplus equation
1961 Westheimer principle
1962 alpha effect nucleophiles (Edwards, J.O./Pearson, R.G.)
1962 discovery of hydrated electron (Hart, E.J./Boag, W.J.)
1962 pulse radiolysis technique (Hart, E.J./Boag, W.J./Dorfman, L.M.)
1963 Pearson's HSAB principle
1963 Cleland rules
1963 Muetterties rule
1963 valence shell electron pair repulsion theory (VSEPR) (Gillespie, R.J.)
1963 Dimroth-Reichardt solvent polarity parameter
1964 Eigen curve
1964 fractionation factor theory (**Kresge, A.J.**/Gold, V.)
1964 density functional theory (Parr, R.G./Yang, W./Kohn, W./**Becke, A.**/Lee, C.)
1965 Woodward-Hoffmann rules
1966 Bunnett-Olsen equations

1966 Hammond-Herkstroeter plot
1966 first report of a laser flash photolysis experiment (Lindqvist, L.)
1967 molecular mechanics calculations (Allinger, N.L.)
1968 Swain-Lupton equation
1968 magic or superacid (**Gillespie, R.J.**/Olah, G.A.)
1969 Edward-Lemieux effect (anomeric effect)
1969 Hansch constant
1969 principle of microscopic reversibility (Ingold, C.K.)
1969 principle of least motion applied to organic reactions (Tee, O.S./Yates, K.)
1969 di-π-methane rearrangement (Zimmerman, H.E.)
1970 More O'Ferrall-Jencks diagram
1970 $S_{RN}1$ aromatic substitution mechanism (Bunnett, J.F.)
1970 factor analysis method (Malinowski, E.R.)
1971 host-guest chemistry (Cram, D.J./Lehn, J.M./Pedersen, C.J.)
1972 Ritchie equation
1972 Koppel-Palm solvent parameters
1972 gauche effect (Wolfe, S.)
1973 application of Marcus theory to proton transfer reactions (Kresge, A.J.)
1975 three-phase test for reaction intermediates (Rebek Jr., J.)
1975 Bordwell carbon acidity scale in polar non-hydrogen-bond solvents
1976 Kamlet-Taft solvent parameters
1976 Baldwin's rules
1977 Kaptein-Closs rules
1977 Jencks' clock
1977 concept of philicity of singlet carbenes (Moss, R.A.)
1977 probe technique to observe spectroscopically "invisible" transients (Scaiano, J.C.)
1978 Cox-Yates acidity function
1978 captodative substitution and effect (Viehe, H.G.)
1981 atoms in molecules (AIM) (Bader, R.F.W.)
1981 Keeffe-Jencks equations
1981 two laser-two colour experiment (Bernstein, R.B./Smalley, R.E./ Rentzepis, R.M./ **Scaiano, J.C.**)
1982 proton inventory technique (Schowen, R.L.)
1983 Reichardt's dye
1984 reactivity-selectivity principle (Giese, B.)

1985	principle of non-perfect synchronization (Bernasconi, C.F.)
1986	general valence bond theory (Goddard (III), W.A.)
1988	**Boyd-Edgecombe electronegativity parameters**
1988	**variable Marcus intrinsic barriers for deprotonation of carbon acids (Bunting, J.W./Stefanidis, D.)**
1990	**Lever ligand electrochemical parameters**
1993	**laser drop experiment (Banks, J.T./Scaiano, J.C.)**
1999	**no-barrier multi-dimensional Marcus theory (Guthrie, J.P.)**
2002	first observation of distinct steps in SN1 reaction (Mayr, H.)

[a]Bolded entries represent contributions by scientists working in Canadian universities or at the National Research Council of Canada.

[b]References to original scientific literature are listed below in alphabetical order according to the concept names.

List of references pertaining to Table S1.

A1 and A2 mechanisms
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Woodward, R.B.; Hoffmann, R. *J. Am. Chem. Soc*. **1965**, 87, 2046
Woodward, R.B.; Hoffmann, R. *J. Am. Chem. Soc.* **1965**, 87, 2511
Woodward, R.B.; Hoffmann, R. *Angew. Chem. Int. Engl. Ed.* **1969**, 8, 871

Zimmerman-Traxler transition state
Zimmerman, H.E.; Traxler, M.D. *J. Am. Chem. Soc.* **1957**, 79, 1920

Zucker-Hammett hypothesis
Zucker, L.; Hammett, L.P. *J. Am. Chem. Soc*. **1939**, 61, 2779

Table S2. Glossary of coined terms used in physical organic chemistry.

Coined term	Scientist(s) who coined term	Reference
A1 (acid catalyzed unimolecular) mechanism A2 (acid catalyzed bimolecular) mechanism	Sir Christopher K. Ingold	J.N.E. Day, C.K. Ingold. Trans. Faraday Soc. **37**, 686 (1941).
Acidity function	Louis P. Hammett	H.P. Treffers, L.P. Hammett. J. Am. Chem. Soc. **59**, 1708 (1937).
Anchimeric assistance (neighbouring group participation) Gk: *anchi* + *meros*	Saul Winstein (suggested by Prof. A. P. McKinlay, professor of Classics at UCLA)	S. Winstein, H.J. Lucas, J. Am. Chem. Soc. **61**, 1576 (1939). S. Winstein, G.R. Lindegren. J. Am. Chem. Soc. **175,** 147 (1953).
Aryne	John D. Roberts	J.D. Roberts, H.E. Simmons, L.A. Carlsmith, C.W. Vaughan. J. Am. Chem. Soc. **75,** 3290 (1953).
Axial and equatorial bonds	D.H.R. Barton O. Hassel K.S. Pitzer V. Prelog	D.H.R. Barton, O. Hassel, K.S. Pitzer, V. Prelog. Science **119**, 49 (1954).
B1 (base catalyzed unimolecular) mechanism B2 (base catalyzed bimolecular) mechanism	Sir Christopher K. Ingold	J.N.E. Day, C.K. Ingold. Trans. Faraday Soc. **37**, 686 (1941).
B-strain (bond)	Herbert C. Brown	H.C. Brown. J. Am. Chem. Soc. **67**, 503 (1945). H.C. Brown, H. Bartholomay, M.D. Taylor. J. Am. Chem. Soc. **66**, 435 (1944).
Bridged ion	T.P. Nevell, E. de Salas, C.L. Wilson	T.P. Nevell, E. de Salas, C.L. Wilson. J. Chem. Soc. 1188 (1939).

Bromonium ion	I. Roberts G.E. Kimball	I. Roberts, G.E. Kimball, J. Am. Chem. Soc. **59**, 947 (1937)
Captodative effect Captodative substituent	Hans G. Viehe	L. Stella, Z. Janousek, R. Merenyi, H.G. Viehe. Angew. Chem. Int. Ed. **17**, 691 (1978). H.G. Viehe, R. Merenyi, L. Stella, Z. Janousek. Angew. Chem. Int. Ed. **18**, 917 (1979).
Carbanion	E.S. Wallis F.H. Adams	E.S. Wallis, F.H. Adams, J. Am. Chem. Soc. **55**, 3838 (1933).
Carbene	William von Eggers Doering	W.v.E. Doering, L.H. Knox. J. Am. Chem. Soc. **78**, 4947 (1956).
Carbenoid	Harold Shechter	L. Friedman, H. Shechter. J. Am. Chem. Soc. **81**, 5512 (1959). L. Friedman, H. Shechter. J. Am. Chem. Soc. **82**, 1002 (1960). L. Friedman, H. Shechter. J. Am. Chem. Soc. **83**, 3159 (1961).
	Gerhard L. Closs Robert A. Moss	G.L. Closs, R.A. Moss. J. Am. Chem. Soc. **86**, 4042 (1964).
Carbonium ion	Adolf von Baeyer	A. von Baeyer, V. Villiger. Chem. Ber. **35**, 1189 (1902). A. von Baeyer. Chem. Ber. **38**, 569 (1905).
Carbocation Carbonium ion Carbenium ion	W. Dilthey (carbenium) George Olah (new definitions)	W. Dilthey, G. Dinklage. Chem. Ber. **62**, 1834 (1929). G. Olah. J. Am. Chem. Soc. **94**, 808 (1972).
Carbyne	Ernst O. Fischer	E.O. Fischer, G. Kreis, K. Kreiter, G. Cornelius, J. Mueller, G. Huttner, H. Lorenz. Angew. Chem. **85**, 618 (1973). E.O. Fischer, G. Kreis, F. Kreissl, W. Kalbfus, E. Winkler, E. J. Organometallic Chem. **65**, C53 (1974).
Catalysis	Jakob J. Berzelius Wilhelm Ostwald	J.J. Berzelius. Jahresberichte **15**, 237 (1835). W. Ostwald. J. Prakt. Chem. **27**, 1 (1883).
Cine substitution	Joseph F. Bunnett R.E. Zahler	J.F. Bunnett, R.E. Zahler. Chem. Rev. **49**, 273 (1951)
Conformation	Walter N. Haworth	W.H. Haworth. The Constitution of the Sugars. Edward Arnold & Co., London. 1929. p. 90.

Covalent	Irving Langmuir	I. Langmuir. J. Am. Chem. Soc. **38**, 2221 (1916). I. Langmuir. J. Am. Chem. Soc. **41**, 868 (1919). I. Langmuir. J. Am. Chem. Soc.**41**, 1543 (1919). I. Langmuir. J. Am. Chem. Soc. **42**, 274 (1920).
Cross-over experiment	Charles D. Hurd	C.D. Hurd, L. Schmerling. J. Am. Chem. Soc. **59**, 107 (1937)
Curly arrow notation (for reaction mechanisms)	Sir Robert Robinson William Ogilvy Kermack	W.O. Kermack, R. Robinson, J. Chem. Soc. 121, 427 (1922). R. Robinson. Two Lectures on an Outline of an Electrochemical (Electronic) Theory of the Course of Organic Reactions. Institute of Chemistry of Gr. Britain & Ireland, London. 1932.
Dipole	Peter Debye	P. Debye. Physik. Z. **13**, 97 (1912)
Distonic radical cation (Gk: diestos = separate) (Latin: distans = separate)	Leo Radom	B.F. Yates, W.J. Bouma, L. Radom. J. Am. Chem. Soc. **106**, 5805 (1984)
E1 (elimination unimolecular) E2 (elimination bimolecular) mechanisms	Sir Christopher K. Ingold Edward D. Hughes	M.L. Dhar, E.D. Hughes, C.K. Ingold, A.M.M. Mandour, G.A. Maw, L.I. Woolf. J. Chem. Soc. 2093 (1948). E.D. Hughes, B.J. MacNulty. J. Chem. Soc. 1283 (1937). E.D. Hughes, C.K. Ingold, A.D. Scott. J. Chem. Soc. 1271 (1937). E.D. Hughes, C.K. Ingold. Trans. Faraday Soc. **37**, 657 (1941). C.K. Ingold. Structure and Mechanism in Organic Chemistry. Cornell University Press, Ithaca. 1953. Chapter 8.
E1cb (elimination unimolecular carbanion) mechanism	Sir Christopher K. Ingold Edward D. Hughes	E.D. Hughes, C.K. Ingold. J. Chem. Soc. 523 (1933); E.D. Hughes, C.K. Ingold, C.S. Patel. J. Chem. Soc. 526 (1933). C.K. Ingold. Structure and Mechanism in Organic Chemistry. Cornell University Press, Ithaca. 1953. Chapter 8.

F-strain (force)	Herbert C. Brown	H.C. Brown. J. Am. Chem. Soc. **67**, 374 (1945). H.C. Brown. J. Am. Chem. Soc. **67**, 378 (1945). H.C. Brown. J. Am. Chem. Soc. **67**, 1452 (1945). H.C. Brown. J. Am. Chem. Soc. **67**, 1765 (1945).
Fast reactions	Manfred Eigen	G. Bunau, M. Eigen. Z. Physik. Chem. **7**, 108 (1956). (first occurrence of phrase)
Flash photolysis	Lord George Porter	G. Porter. Proc. Roy. Soc. London **200A**, 284 (1950). G. Porter. Disc. Faraday Soc. **9**, 60 (1950).
Frangomeric effect	Cyril A. Grob	C.A. Grob. Angew. Chem. Int. Ed. **15**, 569 (1976).
Gauche effect	Saul Wolfe	S. Wolfe. Acc. Chem. Res. **5**, 102 (1972).
Hard and soft acids and bases	Ralph G. Pearson (suggested by Daryle Hadley Busch)	R.G. Pearson. J. Am. Chem. Soc. **85**, 3533 (1963).
Homoaromaticity Homoconjugation	Saul Winstein	S. Winstein. J. Am. Chem. Soc. **81**, 6524 (1959). S. Winstein, L. De Vries. J. Am. Chem. Soc. **81**, 6523 (1959). S. Winstein, J. Sonnenberg. J. Am. Chem. Soc. **83**, 3235 (1961). S. Winstein, J. Sonnenberg. J. Am. Chem. Soc. **83**, 3244 (1961)
Hybridization	Linus Pauling	L. Pauling. The Nature of the Chemical Bond and the Structure of Molecules and Crystals. Cornell University Press, Ithaca, New York. 1948. pp. 58 – 75
Hydrogen bonding	Wendell M. Latimer W.H. Rodebush	W.M. Latimer, W.H. Rodebush. J. Am. Chem. Soc. **42**, 1419 (1920).
Hyperconjugation	George W. Wheland Michael J.S. Dewar	G.W. Wheland. J. Chem. Phys. **2**, 474 (1934). M.J.S. Dewar. Hyperconjugation. Ronald Press, New York. 1962.
I-strain (internal)	Herbert C. Brown	H.C. Brown, R.S. Fletcher, R.B. Johannesen. J. Am. Chem. Soc. **73**, 212 (1951). H.C. Brown, M. Gerstein. J. Am. Chem. Soc. **72**, 2926 (1950).

Inductive effect	Gilbert N. Lewis	G.N. Lewis. Valence and the Structure of Atoms and Molecules. ACS Monograph, The Chemical Catalog Co., New York. 1923. p. 139.
Internal return	Saul Winstein	S. Winstein, R. Heck. J. Am. Chem. Soc. **74**, 5584 (1952).
Intimate ion pair	Donald J. Cram Saul Winstein	D.J. Cram. J. Am. Chem. Soc. **74,** 2129 (1952). S. Winstein, K. Schreiber. J. Am. Chem. Soc. **74**, 2165 (1952). S. Winstein, E. Clippinger, A.H. Fainberg, G.C. Robinson, S. Winstein, L. De Vries. J. Am. Chem. Soc. **76**, 2597 (1954).
Isobestic point	Alfred Thiel	A. Thiel, A. Dassler, F. Wulfken. Fortschritte Chem. Physik Physik. Chem. **18**, 3 (1924).
Isotope	Frederick Soddy	F. Soddy. J. Chem. Soc. **99**, 72 (1911).
Isotope effect	O. Reitz	O. Reitz. Z. Physik Chem. **A177**, 85 (1936).
Isotopic exchange Isotopic labelling experiment	Harold C. Urey	H.C. Urey, L.J. Grieff. J. Am. Chem. Soc. **57**, 321 (1935). D. Rittenberg, W. Bleakney, H.C. Urey. J. Chem. Phys. **2**, 48 (1934).
Keto Enol	Julius Wilhelm Brühl	J.W. Brühl. J. Prakt. Chem. **50**, 123 (1894).
Linear free energy relationship	Louis P. Hammett	L.P. Hammett. Chem. Rev. **17**, 225 (1935). G.N. Burkhardt. Nature **136**, 684 (1935).
Magic acid	Joachim Lukas (originator of name) Edward M. (Ned) Arnett George A. Olah Ronald J. Gillespie	cited in G.A. Olah. J. Org. Chem. **66**, 5943 (2001). E.M. Arnett, J.J. Burke, J.V. Carter, C.F. Douty. J. Am. Chem. Soc. **94**, 7837 (1972). G.A. Olah, M.B. Comisarow, C.A. Cupas, C.U. Pittman, Jr. J. Am. Chem. Soc. **87**, 2997 (1965). G.A. Olah, J. Lukas. J. Am. Chem. Soc. **89**, 2227 (1967). G.A. Olah, J. Lukas. J. Am. Chem. Soc. **89**, 4739 (1967). G.A. Olah, A. Commeyras. J. Am. Chem. Soc. **91**, 2929 (1969). R.J. Gillespie. Acc. Chem. Res. **1**, 202 (1968).

Matrix isolation	George C. Pimentel George Porter	E. Whittle, D.A. Dows, G.C. Pimentel. J. Chem. Phys. **22,** 1943 (1954). E.D. Becker, G.C. Pimentel. J. Chem. Phys. **25**, 224 (1956). I. Norman, G. Porter. Nature **174**, 58 (1954).
Mero-stabilization	Alan R. Katritzky	R.W. Baldock, P. Hudson, A.R. Katritzky, F. Soti. J. Heterocycles **1**, 67 (1973). R.W. Baldock, P. Hudson, A.R. Katritzky, F. Soti. J. Chem. Soc. Perkin Trans. 1 1422 (1974).
Mesoionic compounds	W. Baker B.R. Brown D.L. Hammick	W. Baker. Endeavour **9**, 35 (1950). B.R. Brown, D.L. Hammick, J. Chem. Soc. 628 (1950).
Mesomeric effect Mesomerism	Sir Christopher K. Ingold	C.K. Ingold. Structure and Mechanism in Organic Chemistry, 2nd ed. Cornell University Press, Ithaca, New York. 1969. p. 72ff, 87.
Metal carbenoid	Gert Koebrich Rolf H. Fischer	G. Koebrich, R.H. Fischer. Chem. Ber. **99**, 1793 (1966). G. Koebrich, R.H. Fischer. Chem. Ber. **101**, 3219 (1968). G. Koebrich, R.H. Fischer. Chem. Ber. **101**, 3208 (1968).
	Hitosi Nozaki Ryoji Noyori	H. Nozaki, R. Noyori, R. Yuki Gosei Kagaku Kyokaishi **24**, 632 (1966).
Metal ketyls	Wilhelm Schlenk	W. Schlenk, T. Weickel. Chem. Ber. **44**, 1182 (1911). W. Schlenk, A. Thal. Chem. Ber. **46**, 2840 (1913).
Metallocarbene	Yves Chauvin	J.P. Soufflet, D. Commereuc, Y. Chauvin. Compt. Rend. Acad. Sci. Ser. C.: Sci. Chim. **276**, 169 (1973).
Mutarotation	Thomas H. Lowry	T.H. Lowry. J. Chem. Soc. **75**, 211 (1899). Cited in W. Pigman, H.S. Isbell. Adv. Carbohydrate Chem. **23**, 11 (1968).
Naked ion	Sture Fronaeus	S. Fronaeus. Acta Chem. Scand. **10**, 492 (1956).
No-barrier theory	J. Peter Guthrie	J.P. Guthrie. Can. J. Chem. **77**, 934 (1999). J.P. Guthrie. ChemPhysChem **4**, 809 (2003).

Non-classical ion	Saul Winstein	S. Winstein, D. Trifan. J. Am. Chem. Soc. **74**, 1154 (1952).
Normal salt effect	Sir Christopher K. Ingold Saul Winstein	L.C. Bateman, M.G. Church, E.D. Hughes, C.K. Ingold, N.A. Taher. J. Chem. Soc. 979 (1940). A.H. Fainberg, S. Winstein. J. Am. Chem. Soc. **78,** 2763 (1956).
Octet rule	Irving Langmuir Gilbert N. Lewis	I. Langmuir. J. Am. Chem. Soc. **38**, 2221 (1916). I. Langmuir. J. Am. Chem. Soc. **41**, 868 (1919). I. Langmuir. J. Am. Chem. Soc. **41**, 1543 (1919). I. Langmuir. J. Am. Chem. Soc. **42**, 274 (1920). G.N. Lewis. Valence and the Structure of Atoms and Molecules. ACS Monograph, The Chemical Catalog Co., New York. 1923.
Optical activity	Jean-Baptiste Biot	J.B. Biot. Mem. Acad. Sci. Inst. **2**, 41 (1819).
Oxocarbon	Robert West	R. West, D.L. Powell. J. Am. Chem. Soc. **85**, 2577 (1963).
Photoaffinity labelling	A.Singh E.R. Thornton Frank H. Westheimer	A. Singh, E.R. Thornton, F.H. Westheimer. J. Biol. Chem. **237**, 3006 (1962).
Photon	Gilbert N. Lewis	G.N. Lewis. Nature **118**, 74 (1926).
Principle of microscopic reversibility	Sir Christopher K. Ingold	C.K. Ingold. Structure and Mechanism in Organic Chemistry, 2nd ed. Cornell University Press, Ithaca, New York. 1969. p. 250 – 251.
Principle of nonperfect synchronization	Claude F. Bernasconi	C.F. Bernasconi. Tetrahedron **41**, 3219 (1985)
Probe technique	Juan C. (Tito) Scaiano	R.D. Small, J.C. Scaiano. J. Am. Chem. Soc. **100**, 296 (1978). H. Paul, R.D. Small, Jr., J.C. Scaiano. J. Am. Chem. Soc. **100**, 4520 (1978). R.D. Small, Jr., J.C. Scaiano. Chem. Phys. Lett. **48**, 354, (1977). J.C. Scaiano. Acc. Chem. Res. **15,** 252 (1982).
Proton inventory technique	Richard L. Schowen	K.B. Schowen, R.L. Schowen. Methods Enzymol. **87C**, 551 (1982).
Pseudorotation	Richard S. Berry	R.S. Berry. J. Chem. Phys. **32**, 933 (1960).

"Push-pull" mechanism	Charles Gardner Swain	C.G. Swain. J. Am. Chem. Soc. **70**, 1119 (1948). C.G. Swain, R.W. Eddy. J. Am. Chem. Soc. **70,** 2989 (1948).
"Push-pull" substitution	Alexander T. Balaban	A.T. Balaban. Rev. Roumaine Chim. **16**, 725 (1971). A.T. Balaban, M.T. Caproiu, N. Negoita, R. Baicau. Tetrahedron **33**, 2249 (1977).
Quantum mechanical tunnelling	Eugene P. Wigner	E.P. Wigner. Z. Physik. Chem. **B19**, 203 (1932).
Radical	Antoine Lavoisier	cited in M. Gomberg. Chem. Rev. **1**, 91 (1924).
Radical anion (anionradikale) Radical cation (kationradikale)	E.Z. Weitz	E.Z. Weitz. Z. Elektrochem. **34**, 538 (1928).
Rate constant	Oscar K. Rice H.C. Ramsperger	O.K. Rice, H.C. Ramsperger, J. Am. Chem. Soc. **49**, 1617 (1927).
Rate controlling step	James B. Conant	J.B. Conant, M.F. Pratt. J. Am. Chem. Soc. **48**, 2468 (1926). J.B. Conant, M.W. Evans. J. Am. Chem. Soc. **51**, 1925 (1929). J.B. Conant, J.G. Aston, C.O. Tongberg. J. Am. Chem. Soc. **52**, 407 (1930).
Rate determining step	W.C. Bray Henry Eyring	E.J. Cuy, W.C. Bray. J. Am. Chem. Soc. **46**, 1786 (1924). H. Eyring. J. Chem. Phys. **3**, 107 (1935).
Rate determining heterolysis	Sir Christopher K. Ingold	E.D. Hughes, C.K. Ingold, R.I. Reed. Nature **158**, 448 (1946).
Rate limiting step	Frank H. Westheimer	F.H. Westheimer, E. Segel, R. Schramm. J. Am. Chem. Soc. **69**, 773 (1947).
Reaction intermediate	James F. Norris Julius Stieglitz	J.F. Norris. Am. Chem. J. **38**, 627 (1907). J. Stieglitz. Am. Chem. J. **21**, 101 (1899).
Reactivity-selectivity principle	Bernd Giese	B. Giese. Acc. Chem. Res. **17**, 438 (1984).

Sigma and pi aromatic complexes	Herbert C. Brown	H.C. Brown, J.D. Brady. J. Am. Chem. Soc. **74**, 3570 (1952). M. Kilpatrick, F.E. Luborsky. J. Am. Chem. Soc. **75**, 577 (1953). G.A. Olah, S.J. Kuhn, A. Pavlath. Nature **178**, 693 (1956). H.C. Brown,L.M. Stock. J. Am. Chem. Soc. **79**, 1421 1957). G.A. Olah, S.J. Kuhn, A. Pavlath. J. Am. Chem. Soc. **80**, 6535 (1958). G.A. Olah, S.J. Kuhn, A. Pavlath. J. Am. Chem. Soc. **80**, 6541 (1958). W.v.E. Doering, M. Saunders, H.G. Boyton, H.W. Earhart, E.F. Wadley, W.R. Edwards, R. Laber. Tetrahedron **4**, 178 (1958).
Sigma bond Pi bond	Robert S. Mulliken Wendell M. Latimer W.F. Libby Odd Hassel Raymond Daudel C.A. Coulson H.C. Longuet-Higgins J.W. Linnett W.E. Moffitt	R.S. Mulliken. Phys. Rev. **32**, 186 (1928). W.M. Latimer, W.F. Libby. J. Chem. Phys. **1**, 133 (1933). H. Buu, R. Daudel. Rec. Trav. Chim. Pays-Bas **65,** 731 (1946). O. Bastiansen, O. Hassel. Tidsskrift for Kjemi, Bergevesen og. Metallurgi **7**, 55 (1947). C.A. Coulson, H.C. Longuet-Higgins. Proc. Roy. Soc. London **193A**, 456 (1948). C.A. Coulson. J. Chim. Phys. Physico-Chim. Biol. **45**, 243 (1948). R.S. Mulliken, C.A. Rieke, D. Orloff, H. Orloff. J. Chem. Phys. **17**, 510 (1949). J.W. Linnett, D.F. Heath, P.J. Wheatley. Trans. Faraday Soc. **45**, 832 (1949). W.E. Moffitt, Proc. Roy. Soc. London **196A**, 510 (1949). R.S. Mulliken. J. Chim. Phys. Physico-Chim. Biol. **46**, 497 (1949). R.S. Mulliken. J. Am. Chem. Soc.**72**, 4493 (1950).
S_N1 (substitution nucleophilic unimolecular) S_N2 (substitution nucleophilic bimolecular) mechanisms	Edward D. Hughes Sir Christopher K. Ingold	J.L. Gleave, E.D. Hughes, C.K. Ingold. J. Chem. Soc. 236 (1935). E.D. Hughes. J. Am. Chem. Soc. **57**, 708 (1935). C.K. Ingold. Chem. Rev. **15**, 225 (1934).

SNR1 (aromatic substitution nucleophilic radical unimolecular)	Joseph F. Bunnett	J.K. Kim, J.F. Bunnett. J. Am. Chem. Soc. **92**, 7463 (1970). .K. Kim, J.F. Bunnett. J. Am. Chem. Soc. **92**, 7464 (1970).
Solvent participation	Saul Winstein	S. Winstein, M. Brown, K.C. Schreiber, A.H. Schlesinger. J. Am. Chem. Soc. **74**, 1140 (1952).
Solvolysis	Louis P. Hammett	J. Steigmann, L.P. Hammett. J. Am. Chem. Soc. **59**, 2536 (1937). J. Steigmann, L.P. Hammett. J. Am. Chem. Soc. **59**, 2542 (1937). J. Steigmann, N.T. Farinacci, L.P. Hammett. J. Am. Chem. Soc. **60**, 3097 (1938).
Special salt effect	Saul Winstein	S. Winstein, E. Clippinger, A.H. Fainberg, G.C. Robinson. J. Am. Chem. Soc. **76**, 2597 (1954).
Stereoelectronic effect	Elias J. Corey	E.J. Corey, R.A. Sneen. J. Am. Chem. Soc. **78**, 6229 (1956).
Strain	Adolf von Baeyer	A. Baeyer. Chem. Ber. **18**, 2277 (1885).
Substituent effect	Louis P. Hammett	L.P. Hammett. J. Am. Chem. Soc. **59**, 96 (1937).
Superacid	James B. Conant	N.F. Hall, J.B. Conant. J. Am. Chem. Soc. **49**, 3047 (1927). J.B. Conant, N.F. Hall. J. Am. Chem. Soc. **49**, 3062 (1927). J.B. Conant, T.H. Werner. J. Am. Chem. Soc. **52**, 4436 (1930).
	Ronald J. Gillespie	R.J. Gillespie. Acc. Chem. Res. **1**, 202 (1968). R.J. Gillespie, T.E. Peel. Adv. Phys. Org. Chem. **9**, 1 (1972). R.J. Gillespie, T.E. Peel. J. Am. Chem. Soc. **95**, 5173 (1973).
Synartetic assistance (neighbouring group participation)	Sir Christopher K. Ingold	C.K. Ingold. Structure and Mechanism in Organic Chemistry, Cornell University Press, Ithaca, New York, 1953. p. 520 - 523.
Tautomer (Gk. *Tauto* (the same) + *meros* (part)	Conrad Laar	C. Laar. Chem. Ber. **18**, 648 (1885). C. Laar. Chem. Ber. **19**, 730 (1886).

Time-resolved spectroscopy	G. Gordon W.M. Cady	G. Gordon, W.M. Cady. J. Opt. Soc. Am. **40**, 852 (1950). (first occurrence of phrase)
Transition state theory	Henry Eyring	H. Eyring. J. Chem. Phys. **3**, 107 (1935).
Triplet state	Gilbert N. Lewis Michael Kasha	G.N. Lewis, M. Kasha. J. Am. Chem. Soc. **66**, 2100 (1944).
Umpolung (dipole inversion)	Dieter Seebach	D. Seebach, M. Kolb. Chem. Ind. 687 (1974). D. Seebach, D. Enders. New Synth. Methods **2**, 65 (1975). D. Seebach. Angew. Chem. **91**, 259 (1979). D. Seebach. Angew. Chem. Int. Ed. **8,** 639 (1969).
Ylide	Georg Wittig	G. Wittig, G. Felletschin. Ann. Chem. **555**, 133 (1944). G. Wittig, R. Mangold, G. Felletschin. Ann. Chem. **560**, 116 (1948). G. Wittig, H. Tenhaeff, W. Schoch, G. Koenig, Ann. Chem. **572,** 1 (1951). G. Wittig. Angew. Chem. **63**, 15 (1951). G. Wittig, G. Acc. Chem. Res. **7**, 6 (1974). G. Wittig. J. Organometallic Chem. **100**, 279 (1975). G. Wittig. Science **210**, 600 (1980).
Ylidion (ylide + ion)	Leo Radom	B.F. Yates, W.J. Bouma, L. Radom. J. Am. Chem. Soc. **106**, 5805 (1984)
Ynol Keteno-ynol isomerism	Charles D. Hurd	R.N. Meinert, C.D. Hurd. J. Am. Chem. Soc. **52**, 4540 (1930)
Zero-point energy	Ekko Oosterhuis	E. Oosterhuis. Physik. Z. **14**, 862 (1913). E. Oosterhuis. Proc. K. Acad. Welenschappen **16**, 432 (1914). A.L. Bernoulli. Z. Elektrochem. Angew. Physik. Chem. **20**, 269 (1914).
Zwitterion	Alfred Thiele	A. Thiele, A. Dassler. Chem. Ber. **56B**, 1667 (1923). A. Thiele, A. Dassler. Chem. Ber. **56B**, 2082 (1923). A. Thiele, A. Dassler. Z. Physik. Chem. **108**, 298 (1924).

Table S3. List of intermediates believed to be involved in library of named organic reactions used in organic synthesis.

Intermediate type	Named organic reaction in organic synthesis
Acetoxonium Ions	Acyl rearrangement, Helferich method, Prévost *trans*-dihydroxylation reaction, Woodward *cis*-dihydroxylation reaction
Acylonium Ions	Ester hydrolysis
Acylium Ions	A(acyl)1/A2 ester hydrolysis, Friedel-Crafts Acylation, Fries rearrangement, Gatterman-Koch reaction, Koch-Haaf reaction
Arylium ions	Bischler-Napieralski synthesis, Gattermann reaction, Sandmeyer reaction, Schiemann reaction
Aziridinium ions	Aziridine synthesis via I-N=C=O, Wenker synthesis of aziridines
Benzyne	Aniline synthesis from chlorobenzene
Biradicals	Bergmann cyclization, Norrish Type I and II reactions, Di-p-methane rearrangement, Paterno-Büchi reaction, Photochemical [2 + 2] cyclizations
Betaines	Horner-Emmons-Wadsworth reaction, Schlosser-Wittig reaction, Wittig reaction
Carbanions	Barbier-Wieland reaction, Benzoin condensation, Cadiot-Chodkiewitz reaction, Chichibabin reaction, Clemmensen reduction, Deprotonation of carbon acids, Dieckmann-Thorpe reaction, Enolate type reactions, E1cb reactions, Fritsch-Buttenberg-Wiechell rearrangement, Grignard reaction, Henry reaction (weak acid conditions), Hoch-Campbell aziridine synthesis, Julia olefination, Kulinkovich reaction, Meisenheimer-Jackson complex generation, Neber rearrangement, Organocuprate conjugate addition, Petasis condensation, Ramberg-Bäckland rearrangement, von Richter reaction, Sanger reaction, Shapiro reaction, Thorpe reaction, Wittig [1,2] rearrangement, Wolff-Kishner reduction, Wurtz-Fittig reaction

Carbenes	Arndt-Eistert reaction, Bamford-Stevens reaction, Ciamician synthesis of pyridines from pyrroles, Clemmensen reduction, Corey-Winter reaction (conjectured cyclic dialkoxycarbene), Cyclopropanation of olefins with diazomethane, Reimer-Tiemann reaction, Vinylogous Wolff rearrangement, Wolff rearrangement
Carbenium Ions (trivalent carbon)	Balaban-Nenitzescu-Praill synthesis of pyrylium salts, Bartlett-Condon-Schneider reaction, Camphene rearrangement, Clemmensen reduction, Finkelstein reaction (SN1), Friedel-Crafts Alkylation, Graham reaction, Koch-Haaf reaction, Kochi reaction, Meyer-Schuster rearrangement, Nametkin rearrangement, Nazarov cyclization, Nenitzescu-Praill pyrylium salt synthesis, Nicholas reaction, Pinacol rearrangement, Prins reaction, Rupe rearrangement, SN1 and E1 reactions, Solvolysis reactions, Wagner-Meerwein rearrangements
Carbenoids (metallocarbenes)	Acyclic diene metathesis (ADMET), Asymmetric ring closure metathesis (ARCM), Doetz reaction, Fischer carbene synthesis, Ring-closing metathesis reactions (RCM), Ring-opening metathesis polymerization (ROMP), Schrock carbene synthesis, Simmons-Smith cyclopropanation, Wulff cyclization
Cumulenes	Arndt-Eistert reaction, Curtius rearrangement, Danheiser alkyne-cyclobutanone cyclization, Danheiser [4 + 4] annulation, Hofmann rearrangement, Lossen rearrangement, Meyer-Schuster rearrangement, Schmidt rearrangement, Vinylogous Wolff rearrangement, Wöhler urea synthesis, Wolff rearrangement
1,2-Dications	Benzidine rearrangement, Wallach rearrangement (Wallach intermediate)
Dioxiranes	Shi asymmetric epoxidation

Enolates	Acetoacetic ester synthesis, Aldol condensation, Baylis-Hillman reaction, Bucherer reaction, Chichibabin pyridine synthesis, Claisen condensation, Claisen-Schmidt condensation, Darzens condensation, Dornow-Wiehler reaction, Dieckmann reaction, Favorskii rearrangement, Feist-Benary synthesis of pyrroles, Forster reaction, Gabriel reaction, Gewald thiophene synthesis, Guareschi-Thorpe condensation, Haloform reaction, Hantzsch dihydropyridine synthesis, Hantzsch synthesis of pyrroles, Hinsberg thiophene synthesis, Hooker oxidation, Knoevenagel condensation, Knorr pyrrole synthesis, Malonic ester synthesis, Michael 1,4-addition, Mukaiyama aldol reaction, Mukaiyama-Michael reaction, Mixed ester synthesis, von Pechmann condensation, Petrenko-Kritschenko reaction, Reformatsky reaction, Robinson annulation, Robinson-Schoepf synthesis of tropane, Sakurai reaction, Stetter reaction, Stobbe condensation, Weiss reaction
Enols	Bischler-Napieralski synthesis, Doebner-Miller reaction, a-halogenation of ketones (Lapworth reaction), Hell-Volhard-Zelinsky reaction, Hooker oxidation, Meyer-Schuster rearrangement, Nazarov cyclization, Norrish Type II reaction, Paal-Knorr synthesis of furans, thiophenes, and pyrroles, Pinner triazine synthesis, Pummerer rearrangement, Rupe rearrangement, Skraup reaction, Synthesis of acetates via oxymercuration, Tishchenko reaction, Vorbrueggen coupling
Halonium Ions	Aziridine synthesis via I-N=C=O, Halogenation of olefins, Prévost *trans*-dihydroxylation reaction, Woodward *cis*-dihydroxylation reaction

Iminium Ions[a]	Betti reaction, Bischler-Napieralski synthesis, Bucherer synthesis of hydantoins, Eschweiler-Clarke reaction, Fischer indole synthesis, Houben-Hoesch reaction, Knoevenagel condensation, Mannich reaction, Petasis condensation, Polonovski reaction, Radziszewski synthesis of imidazoles, Stephen reduction, Stork enamine reaction, Vilsmeier-Haack-Arnold reaction, Wohl degradation, Wolff-Kishner reduction
Mercurinium Ions	Oxymercuration of olefins
Metallocomplexes	Alper carbonylation (Pd), Buchwald-Hartwig cross coupling reaction (Pd), Dötz reaction (Cr), Etard reaction (Cr), Heck coupling (Pd), Hosomi-Sakurai reaction (Ti or Al), Jacobsen epoxidation (Mn), Liebeskind-Srogl coupling (Pd, Cu), Nicholas reaction (Co), Nozaki reaction (Ni, Cr), Pauson-Khand reaction (Co), Reppe synthesis (various), Roelen synthesis (various), Sharpless epoxidation (Ti), Sonogashira reaction (Pd), Stahl's aerobic oxidative amination (Pd), Stille coupling (Pd), Stoltz's aerobic oxidative etherification (Pd), Suzuki coupling (Pd), Tebbe reaction (Ti), Thioketal desulfurization (Ni), Uemura oxidation (Pd), Wacker oxidation (Pd), Wulff cyclization (Cr)
Nitrenes	Curtius rearrangement, Hofmann rearrangement, Lossen rearrangement, McFadyen-Stevens reaction, Schmidt rearrangement, Staudinger reaction
Nitrenium Ions	Graham reaction
Nitrilium Ions	Beckmann rearrangement, Bucherer synthesis of hydantoins, Kiliani- Fischer reaction, Ritter reaction, Strecker amino acid synthesis, Ugi condensation
Nitronium Ion	Electrophilic aromatic nitration
Nitrosonium Ion	Diazotization reaction, Nitroso compound synthesis
Non-classical ions	Non-classical ions in solvolysis reactions (e.g., norbornyl)

Organometallic esters	Criegee glycol cleavage (cyclic lead ester), Hooker oxidation (cyclic manganate ester), Jones oxidation (chromate ester), Lemieux-Johnson oxidation of olefins to 1,2-diols (cyclic osmate ester), Lemieux-Johnson oxidative cleavage of olefins to aldehydes (cyclic osmate ester), Permanganate oxidation of olefins to 1,2-diols (cyclic manganate ester), Sarett procedure (chromate ester), Sharpless oxyamination (cyclic osmate ester/amide), Sharpless-Jacobsen dihydroxylation (cyclic osmate esters)
Oxirenes	Arndt-Eistert synthesis, Wolff rearrangement
Oxonium Ions	Acetal/Ketal hydrolysis, Cyclic ether synthesis (acid catalyzed), Hemiacetal/hemiketal hydrolysis, Hydroperoxide rearrangement, Epoxidation of olefins (Prilezhaev reaction), Epoxide hydrolysis, Epoxide rearrangement, Orthoester modification, Paal-Knorr synthesis of furans, thiophenes, and pyrroles, Pinacol rearrangement, Rubottom oxidation
Ozonides	Harries ozonolysis
Phosphonium ions (tetravalent)	Arbuzov-Michaelis reaction, Mitsunobu reaction
o-Quinoid and p-Quinoid intermediates	Bamberger rearrangement, Betti reaction, Bucherer reaction, Fries rearrangement, Hofmann-Martius rearrangement, Houben-Hoesch reaction, Kolbe synthesis, Nenitzescu indole synthesis, Oppenauer oxidation, Orton rearrangement, von Richter reaction, Vilsmeier-Haack-Arnold reaction
o-Quinonemethides and p-Quinonemethides	Reimer-Tiemann reaction
Radicals (acetoxy)	Borodin-Hunsdiecker reaction, Kochi reaction, Wessely oxidation
Radicals (aryl)	Gomberg-Bachmann reaction, Meerwein arylation reaction, Sandmeyer reaction, Ullmann coupling

Radicals (carbon centred)	Birch reduction, Borodin-Hunsdiecker reaction, Eglinton reaction, Glaser coupling, Gomberg-Bachmann reaction, Kochi reaction, Martynoff rearrangement, Meerwein arylation reaction, Meisenheimer rearrangement, Nieuwland enyne synthesis, Radical dehalogenations, Retro Sommelet-Hauser rearrangement, Synthesis of acetates via oxymercuration, Vinyl ether rearrangement, Wittig [1,2] rearrangement, Wohl-Ziegler bromination, Wurtz-Fittig reaction
Radicals (Group IV centred)	Radical dehalogenations (tin radicals)
Radicals (Group V centred)	Pentazadiene [1,3] rearrangement, Mitsunobu reaction (nitrogen radicals)
Radicals (Group VI centred)	Zincke disulfide cleavage reaction (sulfur radicals)
Radicals (ketyl)	Bouveault-Blanc reaction, Clemmensen reduction, McMurry coupling, Pinacol reaction
Radicals (oxygen centred)	Barton reaction
Radicals (peroxy)	Criegee rearrangement
Radicals (phenoxy)	Wessely oxidation
Radical Anions	Acyloin condensation, Benkeser reduction, Birch reduction, Bouveault-Blanc reaction, Clemmensen reduction, Pinacol reaction, Synthesis of acetates via oxymercuration
Radical Cations	Electron impact (mass spectrometry), Hofmann-Loffler-Freytag reaction
Silylium ions	Fleming oxidation
Sulfonium ions	Corey-Kim oxidation, Pfitzner-Moffatt oxidation, Swern oxidation

Tetrahedral Intermediates	Acetal/ketal formation, Aldol condensation, Arndt-Eistert reaction, Asinger reaction, Baeyer-Villiger oxidation, Bamberger-Goldschmidt synthesis of isoquinolines, Bamberger-Goldschmidt synthesis of 1,2,4-triazines, Bamberger-Goldschmidt synthesis of 1,3,5-triazines, Barbier-Wieland reaction, Baylis-Hillman reaction, Benzylic acid rearrangement, Benzoin condensation, Betti reaction, Biginelli synthesis, Blanc reaction, Bucherer synthesis of hydantoins, Cannizaro reaction, Chichibabin pyridine synthesis, Claisen condensation, Claisen-Schmidt condensation, Corey-Winter reaction, Dakin reaction, Dakin-West reaction, Darzens condensation, Dess-Martin periodinate oxidation, Dieckmann condensation, Döbner-Miller reaction, Dornow-Wiehler reaction, Edman degradation, Eschweiler-Clarke reaction, Feist-Benary synthesis of pyrroles, Fischer esterification, Friedländer synthesis, Gabriel reaction, Grieco condensation, Grignard reaction, Guareschi-Thorpe condensation, Hantzsch dihydropyridine synthesis, Hantzsch synthesis of pyrroles, Hemiacetal/hemiketal formation, Hoch-Campbell aziridine synthesis, Hydride reduction reactions (sodium borohydride, lithium aluminum hydride, Tosyhydrazone reduction, Rosenmund reduction, Borch reduction, Gribble reduction of diaryl ketones, Meerwein-Pondorff-Verly reduction, Midland reduction, Julia olefination, Kiliani-Fischer reaction, Knoevenagel condensation, Leuckart reaction, Marshalk reaction, Mixed ester synthesis, Mukaiyama aldol reaction,

	Nenitzescu-Praill pyrylium salt synthesis, Nozaki reaction, Osazone formation, Paal-Knorr synthesis of furans, thiophenes, and pyrroles, Passerini reaction, Perkin reaction, Perkin rearrangement, Petasis condensation, Pictet-Spengler isoquinoline synthesis, Pellizzari reaction, Petrenko-Kritschenko reaction, Polonovski reaction, Radziszewski synthesis of imidazoles, Reformatsky reaction, Riehm quinoline synthesis, Robinson annulation, Robinson-Schoepf synthesis of tropane, Rothemund reaction, Shapiro reaction, Schiff base imine condensation, Schotten-Baumann reaction, Skraup reaction, Stephen reduction, Stetter reaction, Stobbe condensation, Stork enamine reaction, Strecker amino acid synthesis, Synthesis of carbonate diesters, carbamates (urethanes), and ureas, Tiemann rearrangement, Tishchenko reaction, Transesterification reaction, Ugi condensation, Wharton reaction, Weiss reaction, Willgerodt reaction, Wohl degradation, Wolff-Kishner reduction
Thiooxonium ions	Pummerer rearrangement
Triplet ketones	Norrish Type I and II reactions
Triplet olefins	Photochemical cis-trans isomerization
Vinyl cation	Meyer-Schuster rearrangement (allenyl cation), Rupe rearrangement
Wheland (arenium ion)	Azo coupling reaction (Griess reaction), Bamberger rearrangement, Boyland-Sims oxidation, Dienone-phenol rearrangement, Döbner-Miller reaction, Electrophilic aromatic substitution (aromatic halogenation, nitration, sulfonation), Fischer-Hepp rearrangement, Fleming oxidation, Friedel-Crafts alkylation, Gatterman-Koch reaction, Gomberg-Bachmann reaction
Ylides	Corey-Bakshi-Shibata reduction, Corey-Chaykovsky epoxidation, Corey-Kim oxidation, Corey-Winter reaction, Cornforth rearrangement, Schlosser modification of Wittig reaction, Stevens [1,2] rearrangement, Wittig reaction

Zwitterions	Brook rearrangement, Corey-Chaykovsky epoxidation, Corey-Winter reaction, Radziszewski synthesis of imidazoles, Vinylogous Wolff rearrangement

[a]The following synonyms are discouraged by IUPAC: immonium ion, imonium ion.

Table S4. Named organic reactions that do not have reaction intermediates.

Reaction	Reaction
Allylic rearrangement (E2 type)	Hydrogenolysis of benzyl ethers
Aza-Cope [3,3] rearrangement	Kemp elimination (E2-type)
Chapman rearrangement	Koenigs-Knorr synthesis (SN2)
Chugaev reaction	McLafferty rearrangement
Claisen rearrangement	Menshutkin reaction
Claisen-Ireland rearrangement	Noyori hydrogenation
Cope elimination	Oxy-Cope rearrangement
Cope rearrangement	Payne rearrangement (SN2)
Danishefsky reaction	von Pechmann reaction
Decarbonylation reaction	Peterson olefination under acidic conditions (E2)
Diels-Alder reaction	Photochemical [2 + 2] cyclization
1,3-Dipolar cycloadditions	Pyrolysis of sulfoxides
[1,5]-Ene reaction	Sigmatropic rearrangements
Electrocyclic reactions	Smiles [1,4] rearrangement
Esterification with Diazomethane (SN2)	SN2 reactions
Finkelstein reaction (SN2)	Sulfenate-sulfoxide [2,3] rearrangement
Grob fragmentation (E2)	Tiffeneau-Demjanov reaction (SN2 ring expansion)
Hofmann degradation (E2)	Wawzonek-Yeakey rearrangement
Hydroboration-borane rearrangement	Williamson ether synthesis (SN2)
Hydrogenation of olefins	Zeisel determination (SN2)