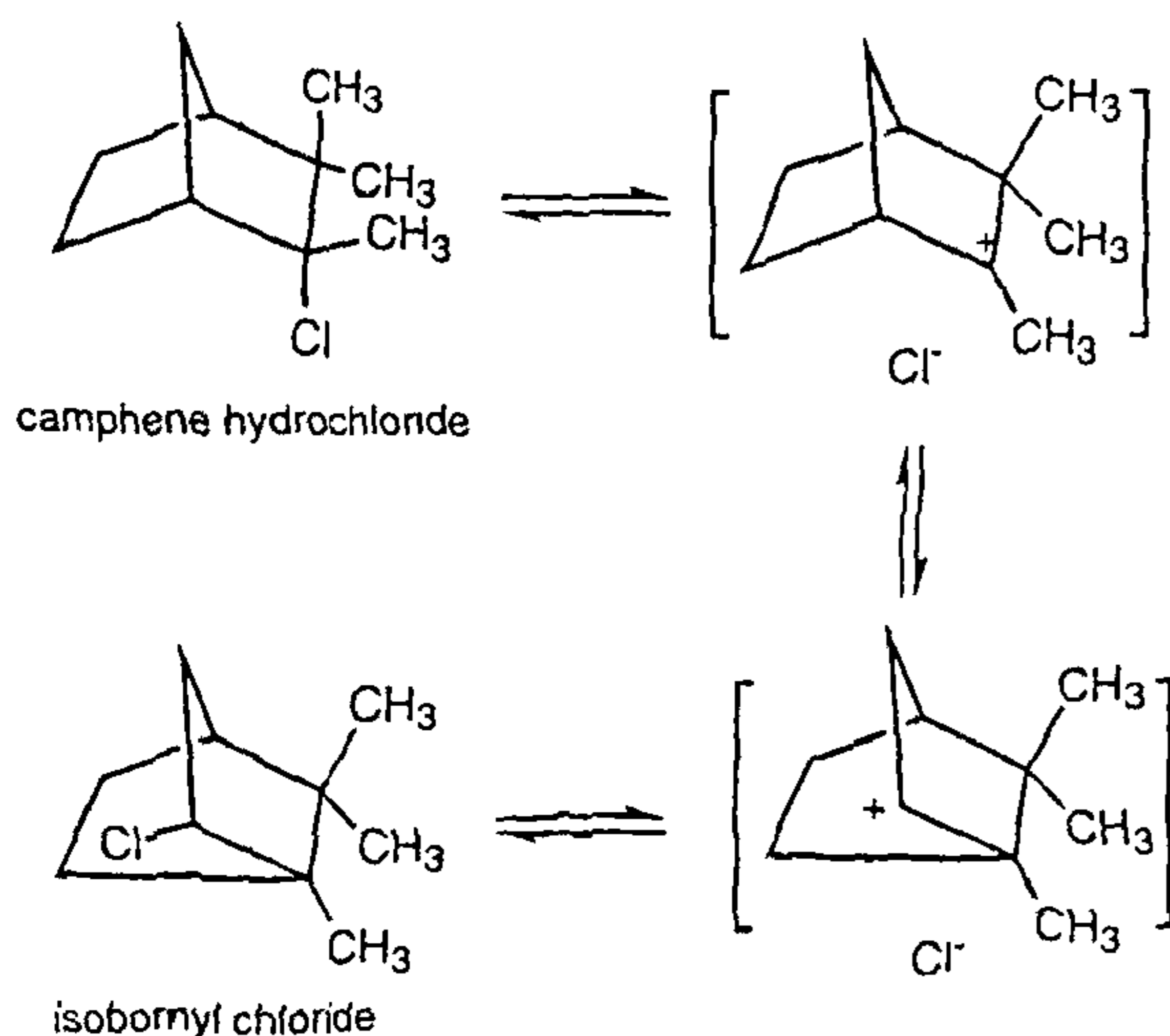


Nobel Prizes 1994: Chemistry

George A. Olah, A superchemist who bestowed long life to fleeting carbocationic intermediates in superacids

One of the most original and daring ideas in organic chemistry was the suggestion that carbocations (positive ions of carbon compounds) might be intermediates in the course of reactions that start from nonionic reactants and lead to nonionic covalent products. Although the nature of triarylmethyl cationic salts and some dyes was known since the pioneering studies of Baeyer, Walden, Gomberg and others at the turn of the twentieth century¹, the more general significance of carbocations in chemistry was for long not recognized. It was Hans Meerwein² who in 1922, while studying the Wagner rearrangement of camphene hydrochloride to isobornyl chloride, found that the rate of the reaction increased with the dielectric constant of the solvent. Further, he found that certain strong Lewis acid chlorides considerably accelerated the rearrangement of camphene hydrochloride to isobornyl chloride. Meerwein concluded that the isomerization actually does not occur by way of migration of the chlorine atom but by a rearrangement of a cationic intermediate. Thus, the modern concept of carbocationic intermediates was born.



Scheme 1.

Ingold, Hughes, and their collaborators in England, beginning in the late 1920s carried out detailed kinetic and stereochemical investigations on what became known as nucleophilic substitution at saturated carbon and polar elimination reactions³. Their work relating to S_N1 and later $E1$ reactions further established the carbocationic concept in organic reactions. Whitmore⁴ in a series of papers in the thirties generalized this

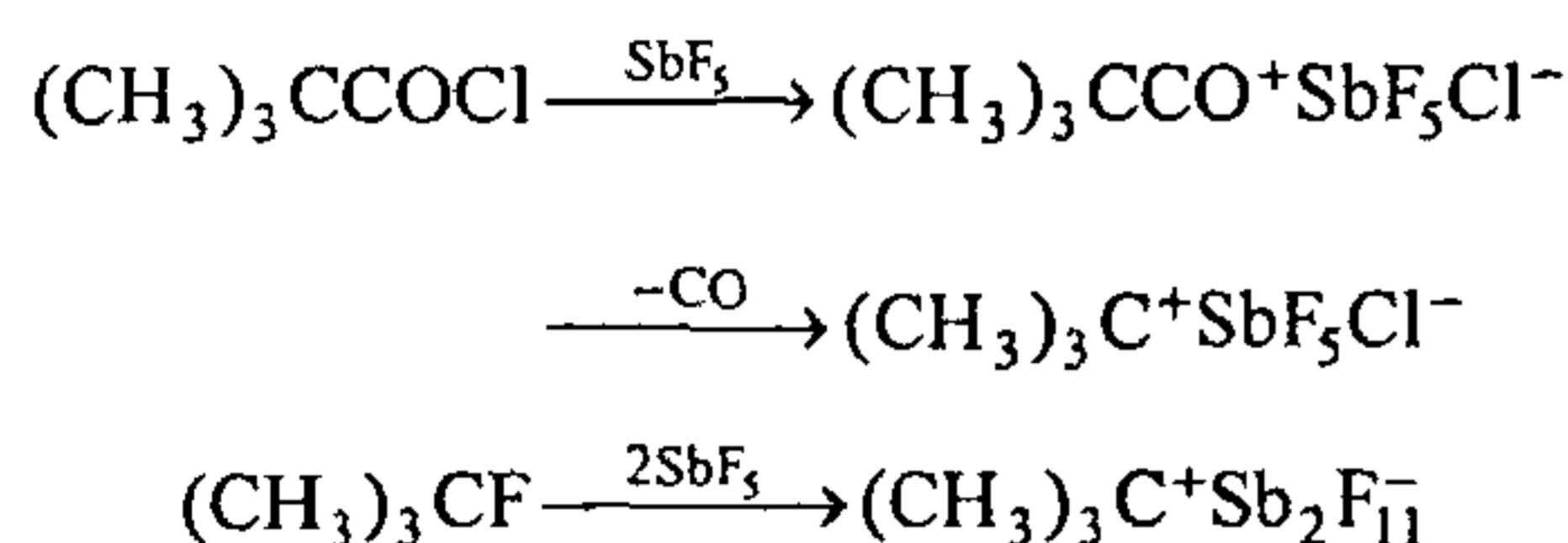
concept to many other organic reactions. Alkyl carbocations, however, were generally considered to be unstable and transient (short lived) as they could not be directly observed in solution chemistry. Many chemists, such as Roger Adams in the United States, consistently doubted their existence as real intermediates. The concept of carbocations slowly grew to maturity through kinetic, stereochemical and product studies of a wide variety of reactions, especially unimolecular nucleophilic substitutions and eliminations. Direct observation of stable, long-lived carbocations, particularly of alkyl cations in the condensed state for long remained an elusive goal till George A. Olah's remarkable discovery in the early sixties.

George Andrew Olah was born in Budapest, Hungary, on 22 May, 1927. His mother was a home maker and father a lawyer. Six days a week, the young Olah attended rigorous German style school. At school he was mesmerized by Hungary's history. Later inspired by talented science teachers he turned his attention to science. After graduating from High School he joined the Technical University of Budapest and began organic chemistry research under the then famous carbohydrate chemist, Geza Zemplén, a student of Emil Fischer. Thus Olah can be considered as the 'Scientific Grandson of Emil Fischer'. At the young and tender age of 22, he obtained the equivalent of a PhD degree at the Technical University and was appointed as an instructor at the Organic Chemical Institute. The same year he married Judith Agnes Lengyel, a dedicated lifelong partner.

At the Organic Chemical Institute Olah became interested in the chemistry of organofluorine compounds. His mentor Zemplén strongly disapproved fluorine chemistry as it involved toxic and noxious reagents such as HF, BF_3 , etc. Eventually Olah prevailed and began his work in the area of alkyl fluorides and acyl fluorides, especially their application in Friedel-Crafts chemistry using a variety of Lewis acids. He also prepared formyl fluoride as well as nitronium tetrafluoroborate ($NO_2^+ BF_4^-$), the latter a versatile electrophilic nitrating agent.

Olah was fascinated by the work of Meerwein⁵, who had earlier in the forties prepared oxonium and carboxonium salts. Even today Olah considers Meerwein as his hero⁶. He was also stimulated by the work of Seel, who for the first time had isolated acylium ($CH_3CO^+ BF_4^-$) salts⁷. At Hungary, he soon rose through the ranks to become the Associate Scientific Director of the Central Research Institute of the Hungarian Academy of Sciences.

Olah with his family left Hungary in 1956 during the Soviet invasion and emigrated to Canada through the help of Judith's relatives and joined the Dow Chemical Research Laboratory at Sarnia, Ontario, Canada, where he continued his research on acyl fluoride-Lewis acid complexes, now employing NMR and IR spectroscopy as analytical tools. A systematic investigation of various Lewis acids led him to antimony pentafluoride, one of the very strong Lewis acids. He also studied pivaloyl fluoride complexes with SbF_5 (ref. 8). The major breakthrough occurred when pivaloyl cation showed tendency for decarbonylation to stable long-lived *tert*-butyl cation. Thus a medium had been found to stabilize elusive alkyl cations⁹.



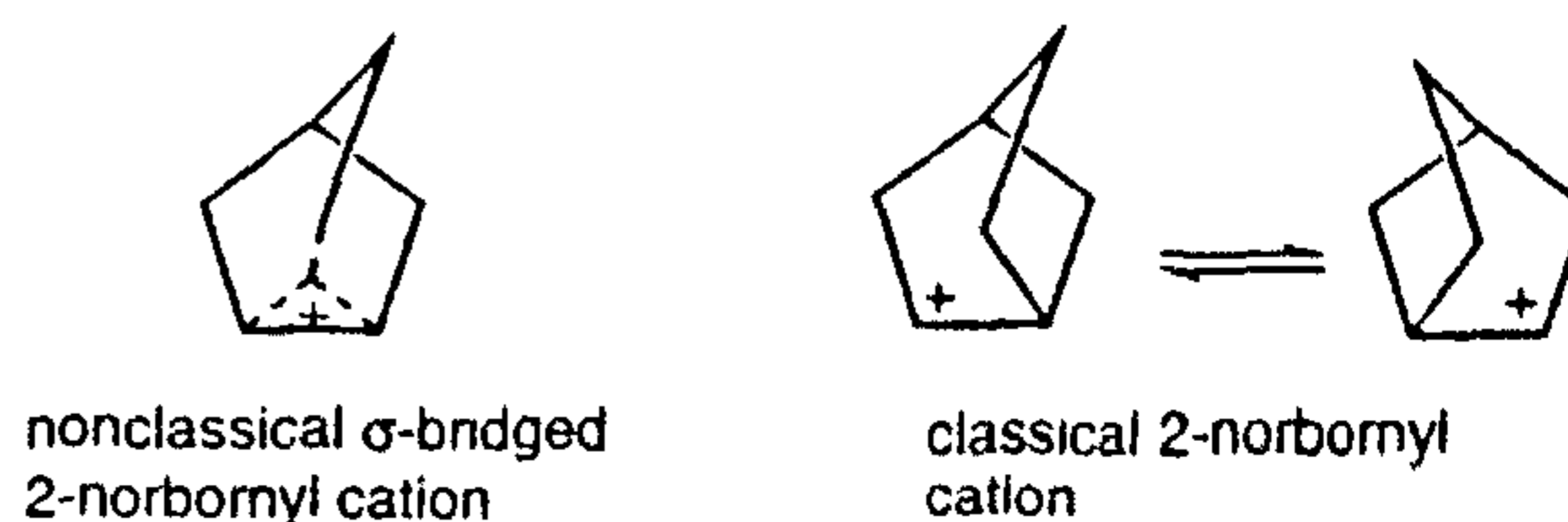
The *tert*-butyl cation was also obtained by dissolving *tert*-butyl fluoride in excess antimony pentafluoride, which served both as the Lewis acid and the solvent. Subsequently, the counter anion was found to be, under these conditions, primarily the dimeric $\text{Sb}_2\text{F}_{11}^-$ anion whereas in $\text{SbF}_5:\text{SO}_2$ and $\text{SbF}_5:\text{SO}_2\text{ClF}$ solutions, both SbF_6^- and $\text{Sb}_2\text{F}_{11}^-$ anions are formed. The possibility of obtaining stable alkyl fluoroantimonate salts from alkyl fluorides and subsequently alkyl chlorides in antimony pentafluoride solution (neat or diluted with SO_2 , SO_2ClF , SO_2F_2 , Freon 11 and Freon 113) or in other superacids such as $\text{HSO}_3\text{F}:\text{SbF}_5$ (named Magic Acid as it can dissolve Christmas candle and produce a solution of long lived *tert*-butyl cation like magic), $\text{HF}:\text{SbF}_5$ (fluoroantimonic acid) $\text{HF}:\text{TaF}_5$ (fluorotantalonic acid), $\text{CF}_3\text{SO}_3\text{H}:\text{B}(\text{OSO}_2\text{CF}_3)_3$ and the like were evaluated in detail, extending studies to all isomeric C_3 - C_8 alkyl halides as well as to a number of higher homologues¹⁰. Using Bronsted superacids stable carbocations were generated from precursors such as alcohols, alkenes, ethers, sulfides, amines and even alkanes. Substrates which possess nonbonded electron pair donors initially form onium ions¹⁰.

To prove that stable alkyl cations, and not exchanging donor-acceptor complexes, were obtained, Olah in addition to ^1H NMR studies also investigated as early as 1962 the ^{13}C NMR of potentially electropositive carbenium carbon atoms in alkyl cations⁹. The ^{13}C NMR chemical shift of the carbocationic center in *tert*-butyl cation in $\text{SbF}_5:\text{SO}_2\text{ClF}$ at -20°C is $\delta^{13}\text{C}$ 335.2 (referenced from the tetramethyl-silane signal), a highly deshielded shift indicating substantial positive charge on the tertiary carbon, with a long range ^{13}C - ^1H NMR coupling constant of 3.6 Hz. The ^{13}C NMR chemical shift of the cationic center in the isopropyl cation

$((\text{CH}_3)_2\text{CH}^+)$ is at $\delta^{13}\text{C}$ 320.6 with a long range coupling of 3.3 Hz. The direct ^{13}C - ^1H coupling constant at the carbocationic center is 169 Hz (indicating sp^2 hybridization of the cationic center). Thus the substitution of the methyl group in the *tert*-butyl cation by hydrogen causes an upfield shift of 14.6 ppm. Such deshielding upon methyl substitution has been attributed to methyl substituent effect. The *tert*-butyl cation is much more stable than secondary isopropyl cation due to additional C-H hyper-conjugation. This effect has been recently demonstrated by the crystal structure analysis of *tert*-butyl cation salt with $\text{Sb}_2\text{F}_{11}^-$ anion¹¹.

The key to Olah's success in the generation and characterization of long lived alkyl carbocations lies in the extremely low nucleophilic nature of the counter anions in the highly acidic superacid medium. Superacids encompass both Bronsted and Lewis acids. Previous attempts to obtain stable alkyl cations in H_2SO_4 had failed because of the relatively nucleophilic nature of HSO_4^- (ref. 12). 100% Sulfuric acid on a Hammett's logarithmic acidity scale, $-\text{H}_0$, has a value of 12. Any Bronsted acid stronger than 100% sulfuric acid is considered as a Bronsted superacid¹³. Thus, FSO_3H ($-\text{H}_0$, 15.1), anhydrous HF ($-\text{H}_0$, 15.1) $\text{CF}_3\text{SO}_3\text{H}$ ($-\text{H}_0$, 14.1), ClSO_3H ($-\text{H}_0$, 13.8) HClO_4 ($-\text{H}_0$, 13.0) are all superacids. Conjugate superacids such as $\text{FSO}_3\text{H}:\text{SbF}_5$ ($-\text{H}_0$, 25) and $\text{HF}:\text{SbF}_5$ ($-\text{H}_0$, 30) are billions and even trillions of times stronger than sulfuric acid. Since no thermodynamic acidity scale exists for Lewis acids any Lewis acid stronger than anhydrous AlCl_3 in its reactivity is considered as a Lewis superacid¹⁰.

Olah's pioneering discovery also led to studies on the 2-norbornyl cation, whose structure was of significant dispute in the early sixties. The much heralded controversy centred around the question whether the experimentally observed significant rate enhancement of the hydrolysis of 2-*exo* over 2-*endo*-norbornyl esters and high *exo* selectivity in the system were due to, as suggested by Winstein, σ -participation of the C_1 - C_6 single bond with delocalization to a bridged 'nonclassical' ion or only by steric hindrance in the case of the *endo*-system and involving only equilibrating 'classical' trivalent ions¹⁴. Nonclassical ions, a term first used by Roberts¹⁵, were suggested by Bartlett^{14a} to contain too few electrons to allow a pair for each bond.



Scheme 2.

Olah came across the 2-norbornyl cation controversy at the 1962 Brookhaven Reaction Mechanism conference where he was invited to unveil his important discovery on the long lived alkyl cations¹⁶. The main event of the meeting was apparently the continuing debate between Winstein and Brown on the classical–nonclassical nature of carbocations (called carbonium ions then) including the 2-norbornyl cation. Olah distinctly remembers to have been called aside separately by both Winstein and Brown and was asked to apply his methods for the structural characterization of the long lived 2-norbornyl cation. In 1964 Olah was transferred to Dow's Eastern Research Laboratory, Massachusetts and the 2-norbornyl cation work was pursued by initial ¹H NMR studies in cooperation with Paul Schleyer from Princeton and Martin Saunders from Yale¹⁷. In 1965 Olah accepted an invitation to join Cleveland's Western Reserve University and soon was asked to oversee the merger of his department with the chemistry department of the adjoining Case Institute of Technology. His handling of the marriage became a role model for complete merger of the two schools, creating the well known and well reputed Case Western Reserve University. It took, however, till 1969 following his move to develop efficient low temperature techniques using solvents such as SO₂ClF and SO₂F₂, to be able to obtain high resolution ¹H and ¹³C NMR spectra of the 2-norbornyl cation eventually down to –159°C in super-cooled solutions, freezing all the degenerate C–C bond (Wagner–Meerwein) and hydride alkyl shifts¹⁸. The studies supported the symmetrical σ -bridged nonclassical structure originally proposed by Winstein. Support for the symmetrical σ -bridged nonclassical structure of the 2-norbornyl cation also comes from Olah's ESCA studies¹⁹, deuterium isotopic perturbation studies²⁰, solid state ¹³C NMR studies at 5 K by Yannoni and Myhre²¹ and *ab initio*/IGLO NMR chemical shift calculations²².

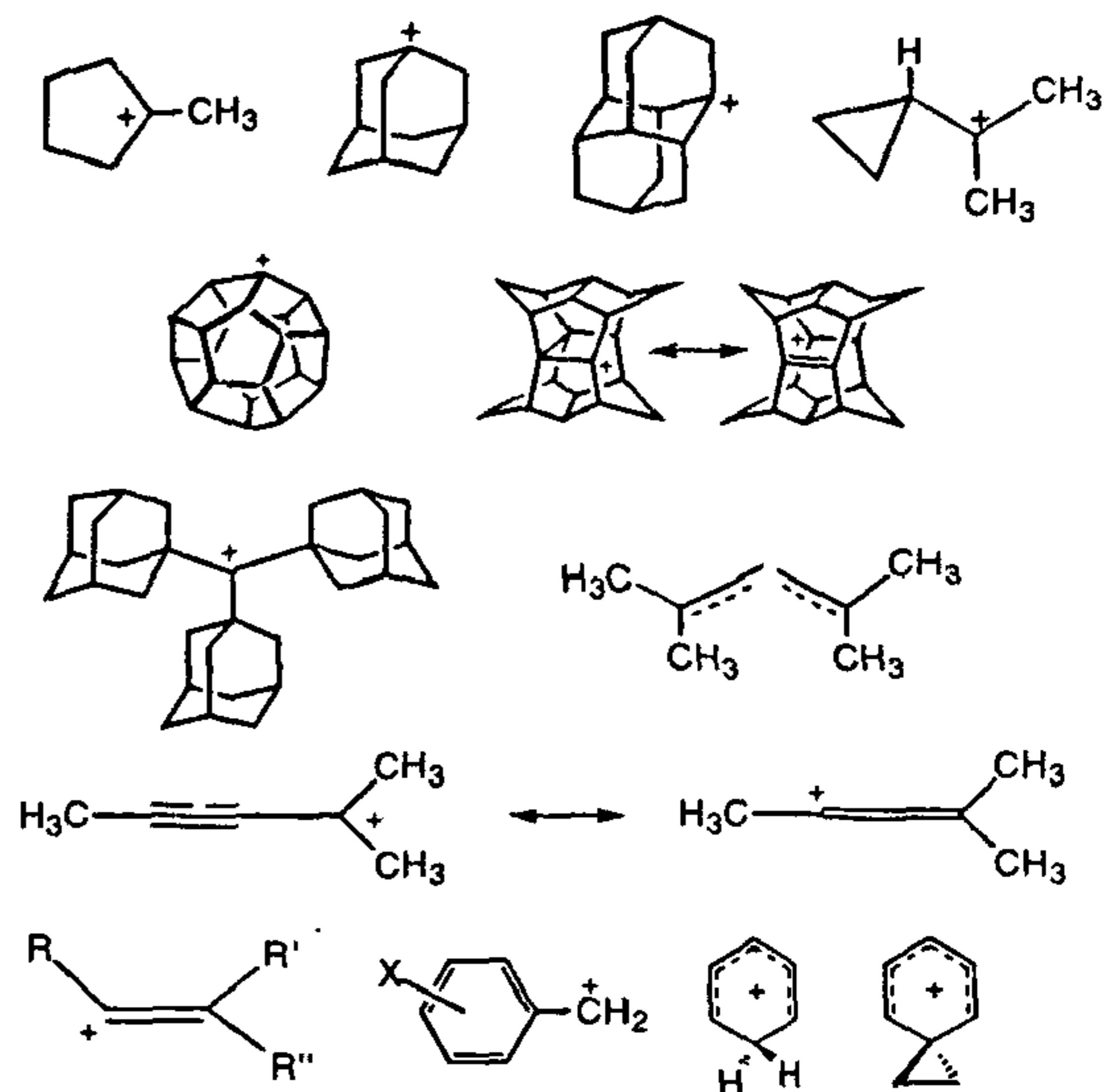
Olah moved to warmer west to University of Southern California at Los Angeles in 1977 and founded the Loker Hydrocarbon Research Institute. As a scientific co-director with the well-known physical chemist Sidney Benson, he established a world renowned center for studies of hydrocarbons.

Since 1960s a wide variety of structurally diverse carbocations, carbodications (for representative examples, see Figure 1) were prepared under so-called long-lived stable ion conditions and characterized primarily by low temperature ¹H and ¹³C NMR spectroscopy¹⁰. In addition to solution NMR studies, solid state NMR, UV-visible, infrared, Raman, ESCA (X-ray photoelectron spectroscopy) and X-ray crystallography have been employed to delineate carbocationic structures, their mode of charge delocalization and stabilization¹⁰.

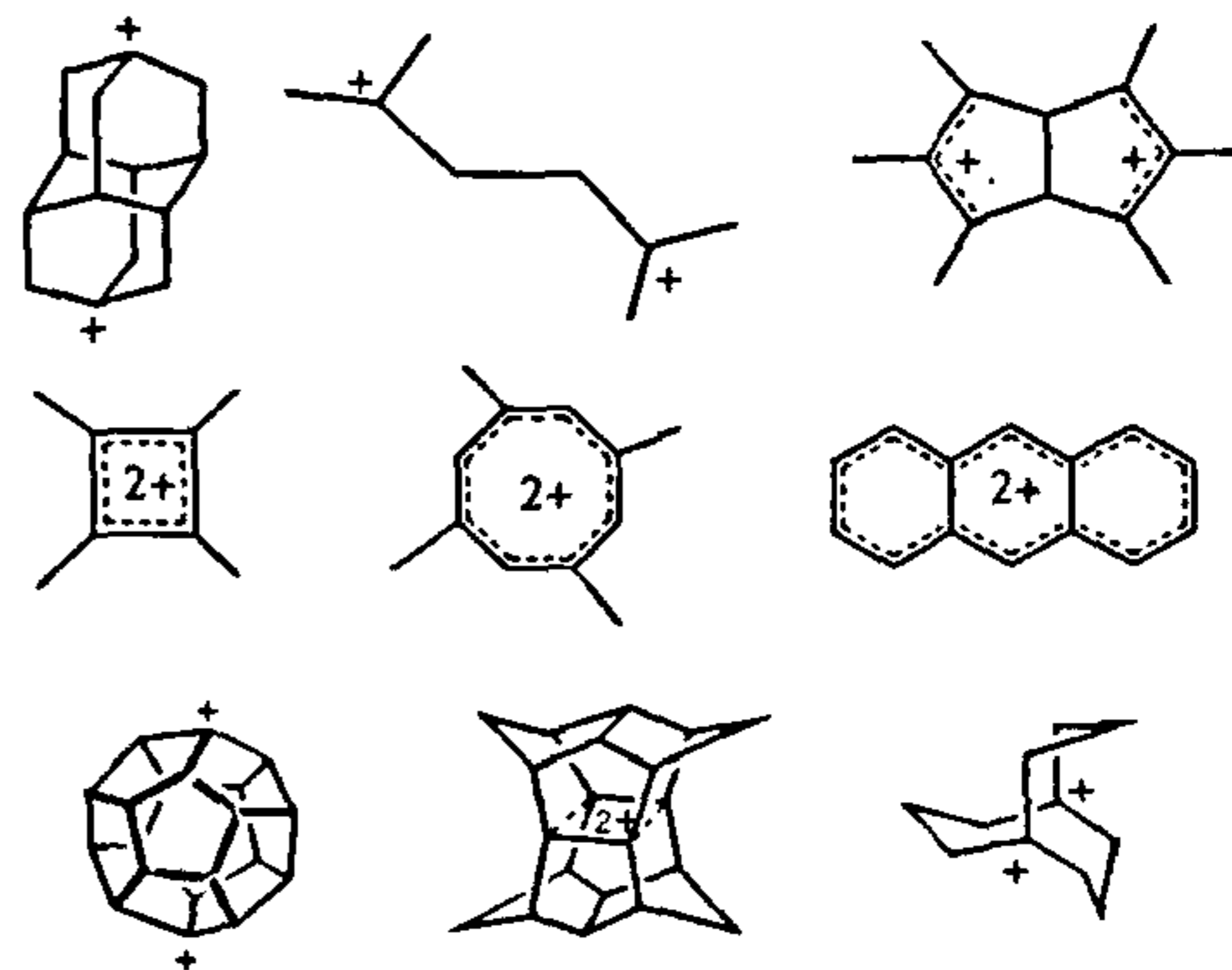
Based on the study of carbocations by direct observation of long-lived species and related superacid

chemistry, it became apparent to Olah that the carbocation bonding concept is wider than previously thought and needed a more general definition which was

Classical Trivalent Carbocations



Carbocations



Scheme 3.

offered by him in 1972 (ref. 23). The definition takes into account the existence of two major limiting classes of carbocations with a continuum of varied degree of delocalization bridging them.

Trivalent {'classical'} carbenium ions contain an sp²-hybridized electron-deficient carbon atom, which tends to be planar in the absence of constraining skeletal rigidity or steric interference (related sp-hybridized, linear oxocarbenium ions and vinyl cations also show substantial electron deficiency on carbon). The carbenium carbon contains six valence electrons, thus is

Equilibrating and Bridged Carbocations and Dications

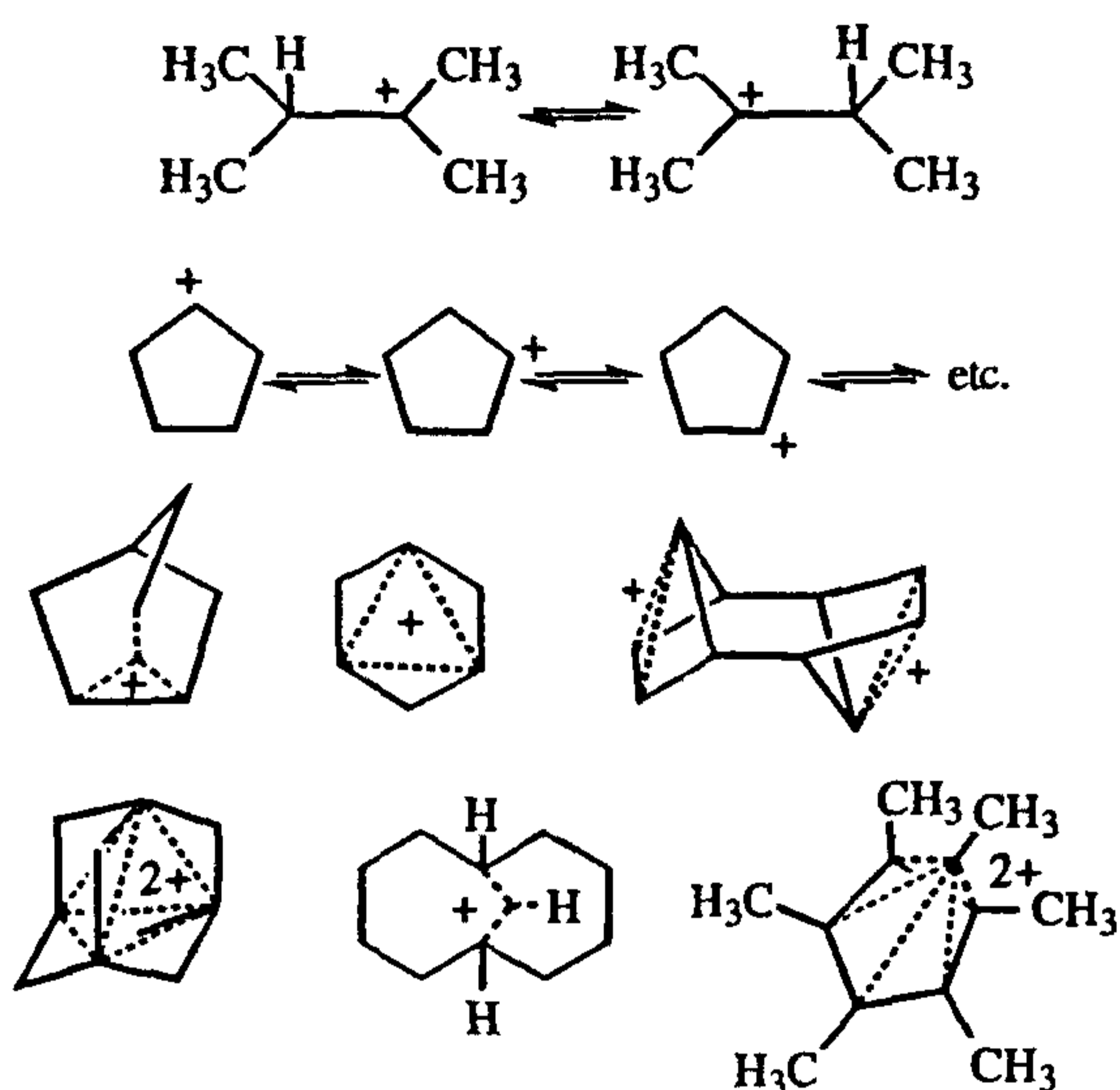
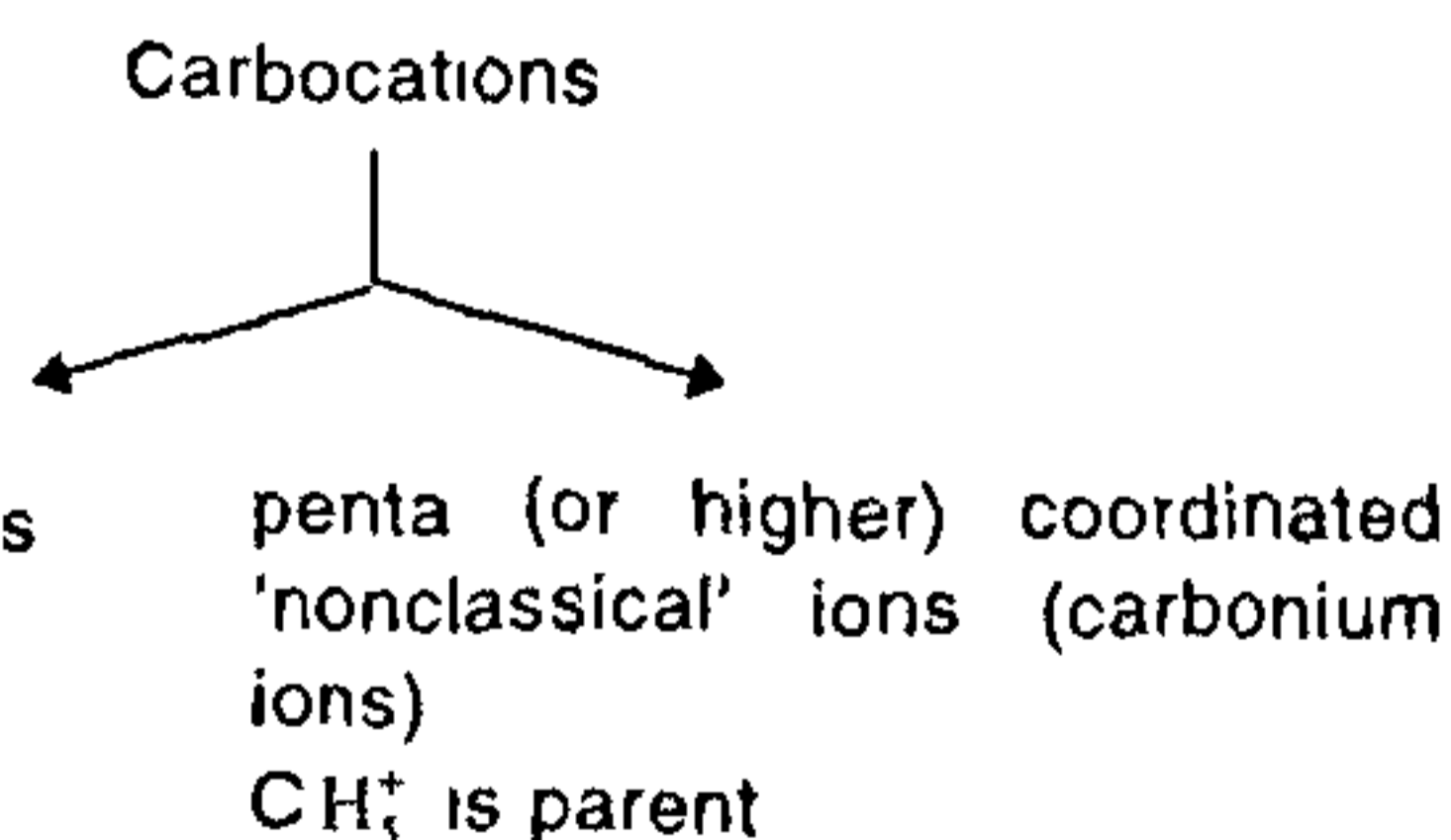


Figure 1. Representative carbocations and carbodications.

highly electron deficient. The structure of trivalent carbocations can always be adequately described by using only two-electron two-center bonds (Lewis valence bond structures). CH_3^+ is the parent for trivalent ions.

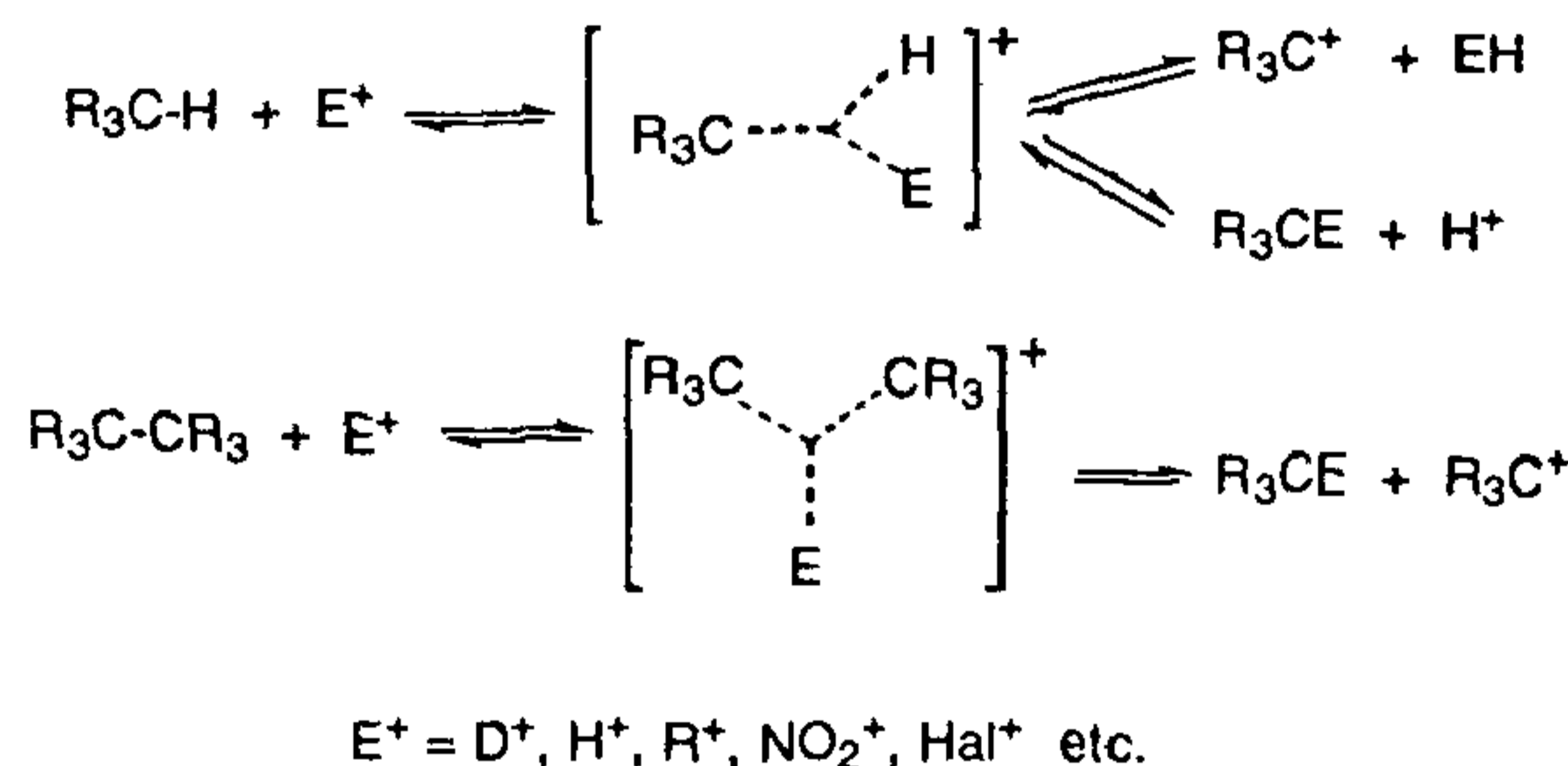
Penta- (or higher) coordinated {'nonclassical'} carbonium ions contain five or (higher) coordinated carbon atoms. They cannot be described by two-electron two-center single bonds alone, but also necessitate the use of two electron three (or multi) center bonding. The carbocation center is always surrounded by eight electrons, but overall the carbonium ion is electron deficient due to sharing of two electrons between three (or more) atoms. CH_3^+ can be considered the parent for carbonium ions.



The most significant aspect of the σ -bridged 2-norbornyl cation structure for Olah was the realization of the ability of C-H and C-C single bonds to act as two

electron donors in electrophilic organic reactions. Two-electron three-center ($2e-3c$) bonding (familiar in boron and organometallic reactions) is involved in these reactions and is the key to much new organic chemistry, i.e. the extended chemistry of hypercoordinated carbon compounds (in short hypercarbon chemistry)²⁴. Trivalent carbenium ions are the key intermediates in electrophilic reactions of π -donor unsaturated hydrocarbons. At the same time pentacoordinated carbonium ions are the key to electrophilic reactions of σ -donor saturated hydrocarbons (C-H or C-C single bonds).

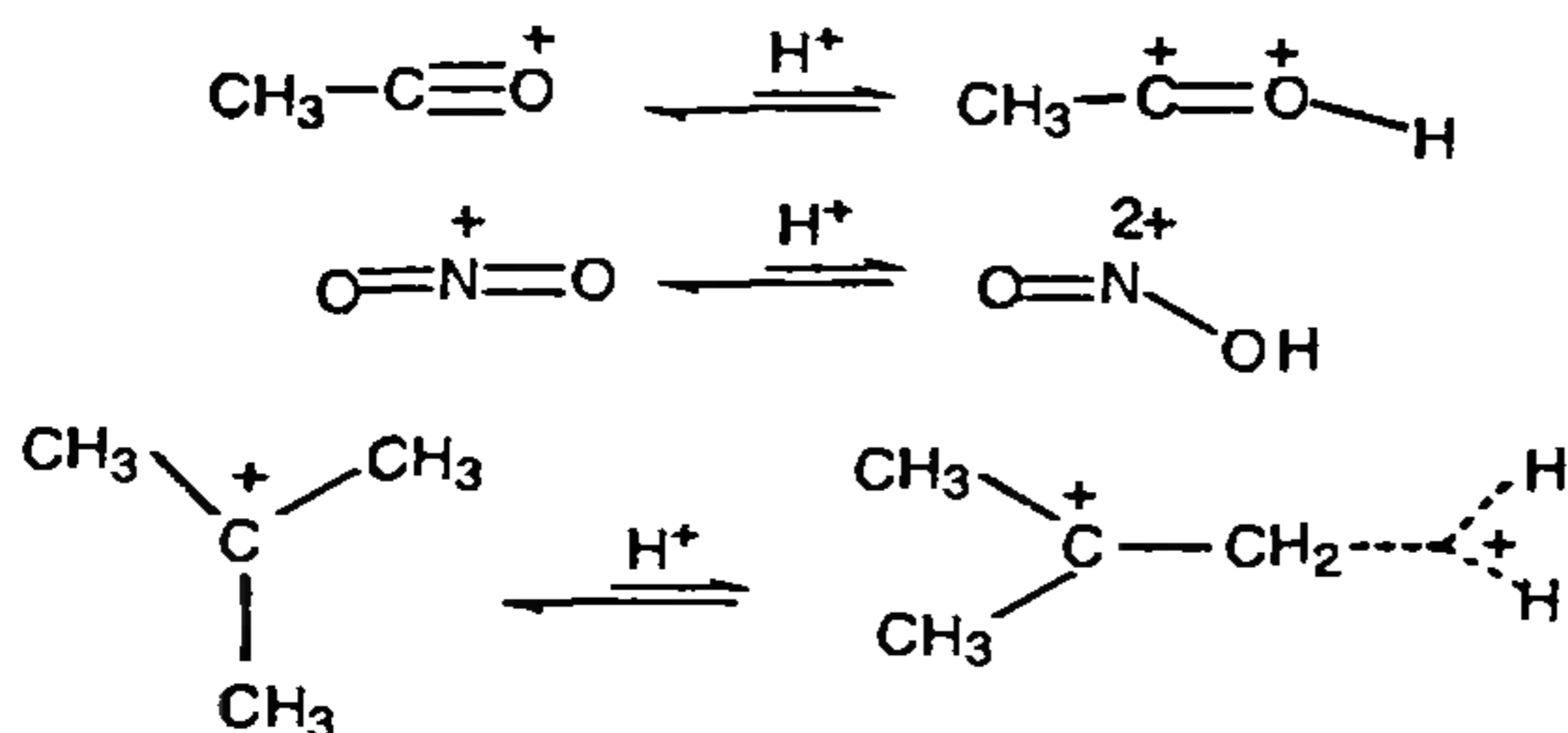
Olah's studies in the late sixties, seventies and eighties for the first time provided evidence for the general reactivity of covalent C-H and C-C single bonds of alkanes and cycloalkanes in various protolytic processes as well as in hydrogen-deuterium exchange, alkylation, nitration, halogenation, etc. This reactivity is due to the σ -donor ability (sigma basicity) of single bonds allowing bonded electron pairs to share their electron pairs with an electron deficient reagent via two-electron, three-center bond formation. The reactivity of single bonds thus stems from their ability to participate in the formation of pentacoordinated carbonium ions. Subsequent cleavage of the three-center bond in the case of C-H reaction results in the formation of substitution products, C-C reaction results in bond cleavage and formation of a fragment carbenium ion, which then can react further.



Scheme 4.

Superacid catalysed hydrocarbon chemistry involving conditions favoring carbocationic intermediates has also gained significance in practical applications¹⁰. Relatively low temperature effective isomerization of alkanes, much improved and environmentally adaptable alkylation, new approaches to the functionalization of methane and possibilities in its utilization as a building block for higher hydrocarbons and their derivatives, as well as moderate conditions for coal liquefaction are some of the few notable examples. Superacidic systems are not limited to solution chemistry. Solid superacids, possessing both Bronsted and Lewis acid sites, are of increasing significance. They range from supported or intercalated systems, to highly acidic perfluorinated resinsulfonic acids (such as Nafion-H and its analogs), to certain zeolites (such as H-ZSM-5) (ref. 10).

Olah has recently realized that electrophiles capable of further interaction (coordination, solvation) with strong Bronsted or Lewis acids can be greatly activated²⁵. The resulting enhancement of reactivity can be very significant compared to that of the parent electrophiles under conventional conditions and indicates superelectrophile formations, i.e. electrophiles with greatly enhanced electron deficiency (frequently of dipositive nature). Common electrophiles such as the acetyl cation, nitronium ion and even *tert*-butyl cation²⁶ are protonated in superacidic media into doubly charged superelectrophiles.



Scheme 5.

The broad implication of such a proposal is only being realized now in practical reactions. In comparison with solution chemistry it is reasonable that in solid superacid catalyst systems, bi- or multidentate interactions forming highly reactive intermediates is possible. This amounts to the solid-state equivalent of protosolvation (protonation). Nature is able to perform its own transformations in ways which chemists have only begun to understand and cannot yet come close to duplicate. At enzymatic sites many significant transformations take place which are acid catalysed (including electron-deficient metal-ion-catalysed processes). Because of the unique geometry involved at enzymatic sites bi- and multidentate interactions must be possible; the superelectrophile concepts developed by Olah may also have relevance to our understanding of some enzymatic processes²⁵.

Olah's chemistry is not just limited to the study of superacids, structural-mechanistic studies, or the development of new hydrocarbon chemistry for which the 1994 Nobel Prize was bestowed. He was also instrumental in the development of new synthetic reagents which have gained wide application in both organic and inorganic chemistry²⁷. Besides carbocation, halonium, nitronium, hydroperoxonium, ozonium salts other reagents include nitronium, nitrosonium salts, pyridinium polyhydrogen fluoride (a versatile fluorinating agent), iodotrimethylsilane, *N*-formyl piperidine, cyanuric fluoride, uranium hexafluoride, selenium tetrafluoride, etc. Olah's pioneering chemistry cuts across the conventional boundary of organic and

inorganic chemistry. His methods are widely used by every day working chemists around the world and form standard part of elementary textbooks in both organic and inorganic chemistry. Olah is a prolific writer. He has published more than 1000 scientific papers, holds 100 patents and has been an author/coauthor of more than 15 books and monographs. He has directed more than sixty doctoral students and has been associated with more than 150 postdoctoral associates whom he has attracted from all over the world. He is one of the most cited authors in the field of organic chemistry today. The astounding volume of fundamental work that has come out of his laboratory is a true inspiration to his students and peers alike.

Apart from the Nobel Prize Olah's work has been recognized by many honors and awards. He is the winner of the American Chemical Society's Award for Petroleum Chemistry, Creativity in Synthetic Organic Chemistry, Roger Adam's Medal, Michaelson-Morley Award, Chemical Pioneer Award, California Scientist of the Year, etc. He is a member of the US National Academy of Sciences and has received honorary doctoral degrees from Durham, Munich, Budapest and Crete. Olah is married to Judith for the past 45 years who is also a well-known chemist in her own right. They have two sons and a grandson.

Olah continues to be a source of new ideas and innovative contributions to chemistry. Olah wrote more than twenty years ago that his realization of the electron donor ability of shared (bonded) electron pairs (single bonds) could one day rank equal in importance with G. N. Lewis' realization of donor ability of the unshared (non-bonded) electron pairs. The fundamental studies of Lipscomb established the structural aspects of boranes through the concept of two-electron three or multi center bonding²⁴. Although the concept of the tetravalency of carbon stated by Kekulé well over a century ago remains an essential foundation of organic chemistry and carbon



Author Prakash with the Nobelist Olah. The photograph was taken on the day the Nobel Prize was announced.

as a first row element cannot extend its valence shell and the octet rule allows formation of only four two-electron two-center (2e-2c) Lewis type bonds, Olah's work clearly established that electron pair of carbon-carbon bond can be involved in two electron-three center (2e-3c) or 2e-multicenter bonding. The hypercoordinate carbocations are 8e carbon systems and do not violate the octet rule (on the other hand, carbanionic S_N2 transition states $[Y-CR_3-X]^-$ are 10e systems and thus cannot be intermediates). This allows carbon to simultaneously bond five (or even six) atoms or groups which is the key to understand the rapidly emerging electrophilic chemistry of saturated hydrocarbons, including parent methane and that of C-H and C-C bonds in general. Thus Olah's work leaves a lasting impact on chemistry.

- 1 a) Norris, J. F., *Am Chem J.*, 1901, **25**, 117, b) Kehrman, F. and Wentzel, F., *Chem. Ber.*, 1901, **34**, 3815; c) Baeyer, A. and Villiger, V., *Chem Ber*, 1902, **35**, 1189, 3013, d) Gomberg, M., *Chem. Ber.*, 1902, **35**, 2397, e) Walden, P., *Chem Ber*, 1902, **35**, 2018, f) Werner, A., *Chem. Ber.*, 1901, **34**, 3300; g) Baeyer, A., *Chem Ber*, 1905, **38**, 569.
- 2 Meerwein, H. and van Emster, K., *Chem. Ber.*, 1922, **55**, 2500
- 3 Ingold, C. K., *Structure and Mechanism in Organic Chemistry*, Cornell University Press, 1953, Ithaca, New York and references therein, 2nd ed, 1969
- 4 Whitmore, F. C., *J. Am. Chem. Soc.*, 1932, **54**, 3274, 3276; *Ann Rep Progr Chem. (Chem Soc. London)*, 1933, **177**, *Chem. Eng News*, 1948, **26**, 668
- 5 Meerwein, H., in *Methoden der Organischen Chemie (Houben-Weyl)*, (ed Müller, E.), 4th ed. vol VI/3, Thieme, Stuttgart 1965 and references therein
- 6 For Olah's recollection see, *Topics in Current Chemistry*, vol. 80, 'In memory of H. L. Meerwein', Springer, Heidelberg, 1979, p. 21
- 7 Seel, F., *Z Anorg Allgem. Chem*, 1943, **250**, 331; 1943, **252**, 24
- 8 Olah, G. A., Tolgyesi, W. S., Kuhn, S. J., Moffatt, M. E., Bastien, I. J. and Baker, E. B., *J Am Chem. Soc.*, 1963, **85**, 1328
- 9 Olah, G. A., DeMember, J. R., Commeyras, A. and Briles, J. L., *J Am Chem Soc*, 1971, **93**, 459 and references therein
- 10 Olah, G. A., Prakash, G. K. S. and Sommer, J., *Superacids*, Wiley, New York, 1985.
- 11 Laube, T., *J Am Chem Soc*, 1993, **115**, 7240
- 12 Rosenbaum, J. and Symons, M. C. R., *Proc. Chem Soc (London)*, 1959, **92**, Rosenbaum, J., Rosenbaum, M. and Symons, M. C. R., *Mol Phys*, 1960, **3**, 205, Rosenbaum, J. and Symons, M. C. R., *J Chem. Soc (London)*, 1961, **1**, Finch, A. C. M. and Symons, M. C. R., *J Chem Soc (London)*, 1965, **378**, b) For a summary, see Deno, M. C., *Progr. Phys Org Chem*, 1964, **2**, 129; c) Olah, G. A., Pittman, C. U. Jr., Symons, M. C. R., in *Carbonium Ions* (eds. Olah, G. A. and Schleyer, P. v R.), Wiley, New York, 1968
13. a) Gillespie, R. J., *Acc Chem Res.*, 1968, **1**, 202, b) Gillespie, R. J. and Peel, T. E., *Adv. Phys Org Chem*, 1972, **9**, 1, *idem*, *J Am. Chem. Soc.*, 1973, **95**, 5173; c) Gillespie, R. J., *Can Chem. News*, May 1991, p. 20
14. a) Bartlett, P. D., *Nonclassical Ions*, Benjamin, W. A., New York, 1965; b) Winstein, S., *Quart. Rev (London)*, 1969, **23**, 1411, c) Brown, H. C. (with commentary by P. v R. Schleyer) *The Nonclassical Ion Problem*, Plenum, New York, 1977
15. Roberts, J. D. and Mazur, R. H., *J. Am. Chem. Soc.*, 1951, **73**, 3542.
16. Olah, G. A., Conference Lecture at 9th Reaction Mechanism Conference, Brookhaven, New York, August 1962
17. Saunders, M., Schleyer, P. v R. and Olah, G. A., *J Am. Chem. Soc.*, 1964, **86**, 5680
- 18 a) Olah, G. A., White, A. M., DeMember, J. R., Commeyras, A. and Lui, C. Y., *J. Am. Chem. Soc.*, 1970, **92**, 4627; b) Olah, G. A., Prakash, G. K. S., Arvanaghi, M. and Anet, F. A. L., *J Am. Chem. Soc.*, 1982, **104**, 7105, c) Also see Olah, G. A., Prakash, G. K. S. and Saunders, M., *Acc. Chem Res*, 1983, **16**, 440.
- 19 a) Olah, G. A., Mateescu, G. D., Wilson, L. A. and Gross, M. H., *J. Am. Chem. Soc.*, 1970, **92**, 7231, b) Olah, G. A., Mateescu, G. D. and Riemenschneider, J. L., *J. Am. Chem. Soc.*, 1972; **94**, 2529, c) Johnson, S. A. and Clark, D. T., *J. Am. Chem. Soc.*, 1988, **110**, 4112
20. Saunders, M. and Kates, M. R., *J. Am. Chem. Soc.*, 1980, **102**, 6867.
21. Yannoni, C. S., Macho, V. and Myhre, P. C., *J. Am. Chem. Soc.*, 1982, **104**, 7380
- 22 Schleyer, P. v R. and Sieber, S., *Angew Chem*, 1993, **105**, 1676, *Angew Chem. Int Ed Engl*, 1993, **32**, 1606 and references cited therein
23. Olah, G. A., *J. Am. Chem. Soc.*, 1972, **94**, 808.
- 24 Olah, G. A., Prakash, G. K. S., Williams, R. E., Field, L. D. and Wade, K., *Hypercarbon Chemistry*, Wiley, New York, 1987.
25. Olah, G. A., *Angew Chem*, 1993, **105**, 805; *Angew Chem. Int Ed Engl*, 1993, **32**, 767 and references therein.
26. a) Olah, G. A., Hartz, N., Rasul, G. and Prakash, G. K. S., *J Am. Chem. Soc.*, 1993, **115**, 6985; b) Olah, G. A., Hartz, N., Rasul, G., Prakash, G. K. S., Burkhardt, M. and Lammertsma, K., *J. Am. Chem. Soc.*, 1994, **116**, 3187.
27. a) Prakash, G. K. S. and Olah, G. A., *Proc Indian Acad. Sci. (Chem. Sci)*, 1988, **100**, 143; b) Olah, G. A., Prakash, G. K. S. and Krishnamurti, R., *A Chapter in Advances in Silicon Chemistry* (ed. Larson, G. L.), Jai Press Inc, Greenwich 1991, vol. 1, pp. 1-64, c) Olah, G. A. and Prakash, G. K. S., *A Chapter on Alkanes, Volume* (eds Patai, S. and Rappoport, Z.), Wiley, New York, 1992, Ch. 13; d) Olah, G. A., Krishnamurti, R. and Prakash, G. K. S., in *Comprehensive Organic Synthesis* (ed. Patai, G.), part 1, Pergamon, London, 1991, vol. 3, Section I 8; e) Olah, G. A., Ohannesian, L. and Arvanaghi, M., *Chem Rev*, 1987, **87**, 671.

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