Ask the Historian

The Origins of the Qualifiers Iso-, Neo-, Primary, Secondary and Tertiary

William B. Jensen

Department of Chemistry, University of Cincinnati
Cincinnati, OH 45221-0172

Question

What are the origins of the qualifiers *iso-, neo- primary, secondary*, and *tertiary* in organic nomenclature?

Saverio Sciarra
38 Via Cossidente
Lavello, Italy (PZ) 85024

Answer

The qualifiers *primary*, *secondary*, and *tertiary* were first applied to the classification of the organic amines in 1856 by the French chemist, Charles Gerhardt, in volume four of his famous *Traité de chimie organique* in order to distinguish between amines resulting from the first (*primary*), second (*secondary*), and third (*tertiary)* stages in the progressive substitution of the three hydrogen atoms of the ammonia molecule (NH_3) by various alkyl radicals (1):

> *One might call the nitrogen compounds primary, secondary or tertiary according as they represent the ammonia type with substitution of one, of two, or of three atoms of hydrogen.*

This terminology was extended to the description of alcohols in 1864 by the Russian chemist, Aleksandr Butlerov, who first prepared what is now known as 2-methyl-2-propanol, but which he viewed as "trimethylated methyl alcohol" or "tertiary pseudo butyl alcohol" (2). In other words, his new alcohol corresponded to the third or tertiary stage in the progressive substitution of the three hydrogen atoms on the methyl group of methanol (CH_3OH) just as the tertiary amines did with respect to the three hydrogens of ammonia. From this point of view, what is now known as 2-propanol represented the second stage of this substitution process and thus corresponded to a secondary alcohol, whereas ethanol resulted from the first stage of substitution and thus corresponded to a primary alcohol.

Figure 1. Aleksandr Butlerov (1828-1886).

By the 1920s this terminology had also been transfered from the naming of specific classes of compounds to the naming of the carbon atoms within a given carbon chain or ring, thus giving rise to our current concept of primary (one C-C link), secondary (two C-C links), tertiary (three C-C links) and, by extension, quaternary (four C-C links) carbon centers (4).

The alternative name of isopropyl alcohol for what is now called 2-propanol is derived from a paper on its structure written by the German organic chemist, Hermann Kolbe, in 1862, where he referred to it as "isomeric propyl alcohol" (i.e., as an isomer of normal or 1-propanol) or "isopropyl alcohol" for short (3). According to Crosland (5), the use of the prefix *iso-* to name isomers of known compounds was established before Kolbe applied it to the alcohols, but obviously resulted in ambiguity if more than one isomer was known for the compound in question.

The prefix *neo*-, from the Greek *neos*, meaning "new," was first applied in sciences other than chemistry (e.g., neolithic). Beginning in the 1880s it became fashionable in mineralogy as a way of distinguishing newly discovered varieties of previously known minerals (e.g., neocyanite, neotestite, etc.). It appears to have been first applied in chemistry proper by Auer von Welsbach in 1885 when he succeeded in separating the rare earth didymia into two new fractions, one of which he named neodymia (6). According to both Beilstein and the *Chemischen Central-Blatt*, the qualifier was first applied in organic chemistry in 1898 by the British chemist, Martin Onslow Forster, who used it to name the derivatives of a newly discovered isomer of bornylamine (7). However, as with the prefix *iso*-, use of the prefix *neo-* to distinguish isomers also proved to be a nomenclature dead-end once more than two isomers of the compound in question became known.

Literature Cited

1. C. Gerhardt, *Traité de chimie organique*, Vol. 4, Didot Frères: Paris, 1856, p. 592.
2. A. Butlerov, "Ueber den tertiären Pseudobutylalkohol (den trimethylirten Methylalkohol)," *Zeit. Chem. Pharm.*, **1864**, *7*, 385-402.
3. H. Kolbe, "Ueber die chemische Constitution des aus dem Aceton durch nascirenden Wasserstoff erzeugten Alkohols," *Zeit. Chem. Pharm.*, **1862**, *5*, 687-690.
4. I been unable to locate who first explicitly proposed this extension, but the earliest textbook usage I could find occurs in J. Schmidt, *Kurzes Lehrbuch der organischen Chemie*, Enke: Stuttgart, 1904, p. 76. Mention of the four classes of carbon centers is quite sporadic in the textbook literature through at least the 1950s.
5. M. P. Crosland, *Historical Studies in The Language of Chemistry*, Harvard: Cambridge, MA, 1962, p. 326.
6. C. Auer von Welsbach, "Die Zerlegung des Didyms in seine Elemente," *Monatsh. Chem.*, **1885**, *6*, 477-491. The other fraction was called praseodymia because of the greenish color of its salts. These two fractions contained the elements now known as neodymium and praseodymium.
7. M. O. Forster, "Isomeric Bornylamines," *J. Chem. Soc.*, **1898,** *73*, 386-397.

Do you have a question about the historical origins of a symbol, name, concept or experimental procedure used in your teaching? Address them to Dr. William B. Jensen, Oesper Collections in the History of Chemistry, Department of Chemistry, University of Cincinnati, Cincinnati, OH 45221-0172 or e-mail them to jensenwb@ucmail.uc.edu

Update

Dr. Heinz-Jürgen Wagner of the Universität Paderborn has informed me that he has traced the use of the qualifier *quaternary* to describe a carbon atom bonded to four other carbon atoms to an 1866 paper by Adolf von Baeyer, where one reads:

> *With respect to the bonding of the carbon atoms with one another, these compounds [i.e., the condensed products of acetone] are noteworthy because they contain a carbon atom bound to four other carbon atoms, and if one maintains that it is characteristic of the aliphatic group that an atom will always be bound to another carbon atom using only a single affinity, then one obtains four classes of bonding interactions for carbon in the same:*
>
> *Primary, 1 atom of carbon bound to 1 other*
> *Secondary, 1 atom of carbon bound to 2 others*
> *Tertiary, 1 atom of carbon bound to 3 others*
> *Quaternary, 1 atom of carbon bound to 4 others*

A similar suggestion was made the same year by Charles Friedel and Albert Ladenburg, though they applied the term quaternary to the overall hydrocarbon rather than to the individual carbon centers as was done by von Baeyer.

Dr. Wagner has also traced the prefix *iso-* to an 1833 paper by Gustav Magnus in which he claimed to have made two new organic acids of identical composition. Magnus explicitly used the term isomeric to describe his new compounds, though it had only recently been introduced by Berzelius, and, among several alternative name choices for his products, suggested "Aetherschwefelsäure" or "Aethionsäure" and "Isoätherschwefelsäure" or "Isaethionsäure." Unlike Kolbe, Magnus did not explicitly state that the prefix *iso-* was an abbreviation for isomeric, though there is little doubt that this was his intention, and in any case, it was his second, rather than his first, name choice for the latter compound – isethionic acid – which ultimately entered the chemical literature. Further complications arise from the fact that his two acids were later shown to have different compositions and thus this example seldom appears in historical accounts of isomerism.

* A. Baeyer, "Ueber die Condensationsproducte des Acetone," *Ann. Chem. Pharm.*, **1866**, *140*, 297-306.

* C. Friedel, A. Ladenburg, "Sur une hydrocarbure nouveau," *Comptes rendus*, **1866**, *63*, 1083-1090.

* G. Magnus, "Ueber die Weinschwefelsäure, ihren Einfluss auf die Aetherbildung, und über zwei Säuren ähnlicher Zusammensetzung," *Pogg. Ann. Phys.*, **1833**, *27*, 367-388.