

La química en la historia, para la enseñanza.

# Charles-Adolphe Wurtz

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## Resumen

Charles-Adolphe Wurtz (1817-1884) fue uno de los químicos más importantes del siglo diecinueve y sus investigaciones ejercieron una poderosa influencia en el desarrollo de la química. Su nombre está asociado estrechamente con síntesis químicas muy conocidas de las cuales la más importante es la de alcanos por la acción del sodio sobre sus derivados halogenados. Desarrolló las fórmulas de los ácidos fosforoso e hipofosforoso, descubrió el oxocloruro de fósforo, las aminas, los glicoles y el butanol terciario, un método práctico para la síntesis de ésteres (incluyendo la glicerina), la reacción aldólica, y efectuó un estudio a fondo del ácido láctico. Aparte de estos descubrimientos, jugó un papel importante en el desarrollo de la teoría estructural. Como Decano de la Facultad de Medicina de París y profesor de la Sorbona estuvo en el centro de la reorganización de la educación superior francesa, muchos de cuyos mejores aspectos se conservan hoy en día. Fue uno de los fundadores de la Sociedad Química de Francia y de la Sociedad Francesa para el Avance de la Ciencia.

## Abstract

Charles-Adolphe Wurtz (1817-1884) was one of the most important chemists of the nineteenth century and whose researches exerted a powerful influence in the development of chemistry. His name is closely related to well-known chemical syntheses, the most important one being that of alkanes by the action of sodium on their halogenated derivatives. He developed the formula of phosphorous and hypophosphorous acids, he discovered phosphorus oxychloride, amines, glycols, and *tert*-butanol, a practical method for the synthesis of esters (including glycerine), the aldol reaction, and did an elaborate investigation of lactic acid. In addition to these discoveries, he played a fundamental role in the building of the structural theory. As Dean of the Faculty of Medicine of Paris and Professor at the Sorbonne, he was at the origin of a reorganization of higher education, of which many of its best characteristics are still present. He was one of the founders of the Société

Chimique de France and the Association Française pour l'Avancement des Sciences.

## Life and career

Charles-Adolphe Wurtz (Figure 1) was born in Wolfisheim, a small village near Strasbourg, on November 26, 1817 and died in Paris, on May 12, 1884, the eldest child of the three children of Jean-Jacques Wurtz (1787-1845) and Sophie Kreiss. His father was a Lutheran pastor of considerable literary culture, but with an introvert personality; his mother came from a well-educated family, was particularly cheerful and sweet-tempered and was an intimate friend and confidant of her son until her death in 1878. Sofia's two brothers, Théodore (professor of Greek at the protestant gymnasium and later at the Faculté de Théologie) and Adolphe Kreiss, were frequent visitors to the Wurtz's home and it is very probable that from their contact Adolphe acquired many of the intellectual abilities that he would later show in his academic career.

In 1826 Jean Jacques Wurtz was appointed to the church of Bergzabern in the Palatinate, and shortly thereafter to the church of St. Pierre-le-Jeune in Strasbourg. There, on July 1826, Adolphe entered the local Gymnase Protestant, an institution controlled by the Lutheran Augsburg Confession. According to Carneiro (1993) the Gymnasium had been founded in 1538 by Jean Sturm (1507-1589), a German Lutheran reformed, who advocated and practiced the propagation of knowledge through teaching and publication. This institution was highly regarded in the educational circle; it had resisted several attempts by the Ministry of Instruction to integrate it into the official Lycée program, particularly after the anti clerical atmosphere that was prevalent after the Revolution. The Gymnasium was linked to the Protestant Faculty, which from the previous century had developed a cosmopolitan tradition by attracting European students and professors and whose curriculum integrated music, physical education, languages, and science. Like the majority of the Alsatian bourgeoisie, by enrolling in the Gymnasium, Wurtz benefited from a bilingual education, which provided access to both French and German cultures

In addition to his formal education, in 1828 Wurtz also attended on a voluntary basis a course on botany, which awakened in him an interest in natural history. This interest was complemented by one on

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Figure 1. Charles-Adolphe Wurtz.

the theories of Lorenz Oken (1779-1851), whose book Wurtz enjoyed reading throughout his life (Carneiro, 1993). Oken was a German naturalist whose speculations that plants and animals are made up of tiny living 'infusoria' led to the cell theory (1779-1851).

According to Charles Friedel (1832-1899), Wurtz's classmate and colleague, during the eight years that Adolphe attended the Gymnasium (1826-1834), he worked industriously and steadily at the various subjects taught to him, but did not particularly distinguish himself in any one, although he ob-

tained several prizes for diligence, one for geography, one for memory and elocution, besides mentions for history and geography, for Latin and Greek translation, mathematics, and French verse. These achievements were not enough for his father and led him to remark that he did not expect his son to do anything outstanding in life (Friedel, 1885).

Adolphe left the Gymnase in 1834, after taking the degree of *Bachelier ès Lettres*. His father wanted him to follow his steps and study theology. After much arguing and after being given the choice between religious or medical studies, the young man decided on a medical course at the University of Strasburg. The decision was probably influenced on the one hand by the fact that the curriculum included a fair amount of chemistry and experimental work, and on the other, the advice of his classmate who was destined to be a distinguished chemist and in later years collaborate with Wurtz in the publication of the *Dictionnaire de Chimie* (Wurtz, 1868-1878). In Strasburg, Adolphe was placed with Dr. Schneiter, a friend of the family.

Wurtz soon became (1835) second and before long full assistant in the chemical and pharmaceutical department. After a competitive examination in 1839, he was appointed *Chef des Travaux Chimiques de la Faculté*, on which occasion he wrote the essay *Histoire Chimique de la Bile à l'État Sain et à l'État Pathologique*. He fulfilled the duties of the new post under the direction of Amédée Cailliot (1805-1884) until he left Strasburg (Williamson, 1885).

In August 13, 1843 he took the degree of Doctor of Medicine and on this occasion he read a thesis

*Etudes sur l'Albumine et sur la Fibrine*, which gained him a medal from the Faculty. In his thesis he described a method for the purification of soluble albumin and argued for a difference between albumin of blood and the albumin of an egg (Wurtz, 1844a).

After graduation his father authorized him to go for a year to Giessen, where Justus von Liebig (1803-1873) had opened the first laboratory for students. There he met August Wilhelm Hofmann (1818-1892), who later complemented his work on the amines and became his biographer. Under Liebig's direction Wurtz began his research training with a study of hypophosphorous acid in an attempt to decide between the conflicting interpretation and formulas of Pierre Louis Dulong's (1785-1838) and Heinrich Rose (1795-1864). Impressed by Wurtz's abilities Liebig entrusted him with the translation of some of his papers into French. Wurtz sent these translations to Paris for insertion in the *Annales de Chimie et de Physique*; they were the means of bringing Wurtz into contact with some of the leading French men of science, and in particular with the increasingly powerful Jean-Baptiste Dumas (1800-1884) (Williamson, 1885).

Wurtz completed his *Wanderjahr* in Austria during the autumn of 1842 and returned to Strasburg with letters of recommendation from Liebig. In 1844 he left Strasburg to Paris where he worked for a short time with Antoine Jérôme Balard (1802-1876) at the Sorbonne. Afterwards he transferred to Dumas private laboratory, in the Rue Cuvier, where Auguste Cahours (1834-1910), Hermann Lewy (1813-1878), and Jules Bouis (1822-1886) were also working (Williamson, 1885).

Between 1844 and 1845 Wurtz undertook the translation into German of Charles Frédéric Gerhardt's (1816-1856) first book, *Précis de Chimie Organique*. In this book, Gerhardt introduced the concept of homology (a series of homologues was a series of compounds the successive members of which differed by  $\text{CH}_2$ ) and presented his system of nomenclature and classification (see below). As Gerhardt mentioned, the main difficulty of this translation was that the German systematic names did not express the genus a species to which a compound belonged and that was precisely the novelty of his nomenclature (Carneiro, 1993).

In 1845 Wurtz was appointed Dumas's *préparateur* at the Faculté de Médecine and four years later he took over Dumas course on organic chemistry, who was prevented by his political and administrative occupations from attending to his professional

duties (Williamson, 1885). It was during this stage of his professional life that Wurtz made his great discovery of composite ammonias, which had such an important influence on the progress of chemistry, and which gave him the clue to the constitution of the vegetable alkaloids (Wurtz, 1848a,b; 1849a,b; 1851). It was also at Dumas laboratory that he completed the investigation that he had begun at Giessen on the constitution of the hypophosphites (Wurtz, 1843; 1846a).

From 1845 to 1850 Wurtz held the appointment of Chef de Travaux Chimiques of the 3<sup>rd</sup> and 4<sup>th</sup> year students at the École Centrale des Arts et Manufactures (Williamson, 1885).

After the *suppléance* period to Dumas at the Faculty of Medicine (1849-1853), Wurtz followed his steps and assumed his positions one by one: lecturer in organic chemistry (1849), professor (1853), and Dean of the Faculty (1866). His dedication to the latter job resulted in the creation of a “true school of chemistry” unique in the panorama of nineteenth century French chemistry (Carneiro, 1993). His curriculum reforms led to a significant improvement in the education of medical students and ensured that clinical professors in the hospitals had better laboratory facilities.

When the Institut Agronomique was founded at Versailles in 1850, Wurtz was appointed Professor of Chemistry in it. This appointment was not of long duration because the Prince President (Napoleon III) suppressed it in 1852. He lost this appointment just as he was about to marry (the Institute was re-established in 1877) (Williamson, 1885).

Anyhow, this disappointment was more than compensated by Wurtz's election as professor at the Faculté de Médecine in 1853. Dumas had resigned his chair and Mateu Joseph Bonaventur Orfila (1787-1853), who had been professor of Mineral and Toxicological Chemistry, was dead. The two chairs were now united and Wurtz appointed to the post. Wurtz taught at the École de Médecine for twenty-five years and in 1874 he was appointed to the new Chair of Organic Chemistry, which had been specially created for him at the Sorbonne. He resigned the office of Dean at the École de Médecine but was named Honorary Dean (Williamson, 1885).

Wurtz was doubtless the most famous French chemist of his time and one of the most enthusiastic and outstanding teachers of his generation. Since he spoke French, German, and English, he was able to surround himself with the most distinguished chemists of the day. More than one-hundred French and foreign scientists were formed in his laboratory,

among them Archibald Scott Couper (1831-1892), Friedrich Konrad Beilstein (1832-1906), Alexander Mikhailovich Butlerov (1828-1886), James Mason Crafts (1839-1917), Alexandre Leon Etard (1852-1910), Friedel, Joseph Achilles Le Bel (1847-1930), Edmund von Lippmann (1857-1940), Jean Marcet (1785-1858), Adolphe Perrot (1833-1877), Raoul Pictet (1842-1929), Alexander Saytzeff (1841-1910), Hugo Schiff (1834-1915), Bernard Christian Tollens (1841-1918), Jacobus Henricus van't Hoff (1852-1911), and August von Wassermann (1866-1925). It was in his laboratory that Paul Emile Boisbaudran (1838-1912) discovered gallium in 1875 (André, 1956).

Besides being a brilliant lecturer and laboratory teacher Wurtz excelled as a writer. From 1852 to 1872 he was responsible for the section devoted to foreign literature in the *Annales de Chimie*. He published his *Dictionnaire de Chimie Pure et Appliquée* (Wurtz, 1868-1878) and a book *La Théorie Atomique* (Wurtz, 1879) that went into many translations. In 1864 he published his medical course, in two volumes, under the title *Traité Élémentaire de Chimie Médicale* (Wurtz, 1864-1865), in which he exposed in a critical manner the whole knowledge of chemistry, still maintaining the notation of equivalents, that he had already abandoned in his papers and conferences, but that prepared the ground for the future exposition of atomic notation (André, 1956). The *Leçons Élémentaires de Chimie Moderne* (Wurtz, 1867-1868) is a model of lucid exposition (Williamson, 1885) and in it the notation of equivalents is definitely abandoned in favour of the atomic notation (André, 1956).

Wurtz excelled as a practical chemist and almost all of his contributions left a mark in organic synthesis. He developed and simplified synthetic processes for the production of phosphorus oxychloride, of neurine from ethylene oxide, of aldol from acetaldehyde, of phenol from benzene, and of esters from alkyl halides and the silver salt of acids. Wurtz also carried many experiments regarding the density of vapour capable of dissociation, such as phosphorus pentachloride, chloral hydrate, etc.

About the year 1856 there existed in Paris a society of young chemists, who used to meet for exchange of knowledge and instruction. In 1859 Wurtz was instrumental in transforming this association into a learned society, the *Société Chimique de France*. For this purpose he succeeded in engaging the help of Balard, Marcelin Berthelot (1827-1907), Cahours, Dumas, Henry Sainte-Claire Deville (1818-1881), Louis Pasteur (1822-1895), and others. Although the idea for the *Société Chimique de France* may not have originated

with Wurtz, he became its secretary, its guiding spirit, and several times its President (1864, 1875, 1878). It was during his first presidency (1864) that a number of separate publications, including Wurtz's own *Répertoire de Chimie Pure* (established in 1858) and Charles-Louis Barreswill's (1817-1870) *Répertoire de Chimie Appliquée* were amalgamated to produce the official bulletin of the society. The *Répertoire de Chimie Pure*, gave an abstract of all the French and foreign papers on chemistry similar to that of Barreswill, dedicated to industry. During the year 1863 he gave a series of lectures about different chemical subjects to the Society; these lectures were later published as the book *Philosophie Chimique* (Wurtz, 1864).

Wurtz played an active role in establishing the *Association Française pour l'Avancement des Sciences*, a new organization designed to foster science in the provinces, and modeled after the British Association, with which Wurtz was impressed. The French Association held its first meeting at Bordeaux in 1872. When it met at Lille in 1874, Wurtz delivered the presidential address (Williamson, 1885).

According to Friedel (1885) and Williamson (1885), the many activities that Wurtz took in different fields did not alienate him from the religious beliefs he had been brought up in. He contributed greatly to the reorganization in Paris of the Strasburg *Faculté de Théologie Protestante*. He displayed no trace of anticlericalism and found little difficulty in harmonizing his science with his faith. A staunch defender of the atomic theory against the sceptical positivism of Berthelot, he gave the theory a teleological interpretation in perfect accord with his natural theology. The political and academic power associated with his many administrative and senior academic positions were no factor in his decisions. For example, he defended his socialist colleagues Alfred Naquet (1834-1916)<sup>1</sup> and Françoise Robin (1748-1841), who favored social ideas that were totally against his. His

<sup>1</sup> During the Second Empire Alfred Naquet (1834-1916) was an active representative of the Republican Party. He was a radical, belonging to the extreme left, and an avowed enemy of parliamentary government. He was professor in the Faculty of Medicine in Paris and in Palermo. He lost his professorship in 1867 with his civic rights, when he was condemned to fifteen months' imprisonment for his share in a secret society. On a new prosecution in 1869 for his book *Religion, Propriété, Famille* he fled to Spain. After his return to France he took an active share in the revolution of the 4th of September 1870 and became secretary of the commission of national defence His proposal for the re-establishment of divorce became law in 1884.

liberalism also manifested itself in his campaign for the admission of women students to the classes and examinations of the Faculty of Medicine. After German annexation of his native country Alsace during the Franco-Prussian War led to the displacement of many of his countrymen to Paris, Wurtz worked relentlessly to provide them with help.

On March 17, 1852 Wurtz married Constance Pauline Henriette Oppermann (1830-1906), a well-to-do childhood friend; they had four children, Marie (1854-1930), Lucie (1856-1922), Robert (1858-1919) who became a physician, and Henri (1862-1944) who became an army officer after graduating from the École Polytechnique.

Wurtz passed away at age 67, on May 12, 1884 after a short illness caused by an accidental infection of the bladder and prostate. He was buried in the Père-la-Chaise cemetery.

### Honors and awards

Wurtz received many honors for his contributions to science and public life. He became a member of the Académie de Médecine in 1856 (replacing François Magendie (1783-1855), its Vice President in 1869, and President in 1871. He was admitted to the chemical section of the Académie des Sciences (Institut) in 1867, replacing Théophile Jules Pelouze (1807-1867); he became its Vice President in 1880 and President in 1881.

He was a member of the principal learned and scientific societies, both in France and abroad: Member of the Academies of Berlin, Vienna, Munich, Turin, Venice, Bologna, Upsala, Edinburgh, Lincei of Rome, the Royal Academies of Belgium and Ireland, the Chemical Society of London, the Science Societies of Holland, Goettingen, Trieste, the Société Industrielle de Mulhouse, etc. (Friedel, 1885). He became a Foreign Member of the Royal Society before he was admitted to the Institut. In 1873 he was elected corresponding member of the Académie des Sciences of Saint Petersburg (Williamson, 1885).

In 1859 the Académie awarded him jointly with Cahours the Jecker Prize (for research in organic chemistry); in 1864 the prize was again conferred on him. In 1865 the Institut bestowed on him the great Biennial Prize (Napoleon III Prize) of 20,000 francs and in 1881 the Royal Society awarded him the Copley Medal (Williamson, 1885).

Among the many decorations he received are: Chevalier d'Isabelle la Catholique d'Espagne et du Christ du Portugal, Commandeur de la Rose of

Brazil, and Order of François-Joseph of Austria (Friedel, 1885).

In 1875 he was appointed Maire of the VII<sup>e</sup> Arrondissement of Paris, until 1881 when he was elected to the Senate, in representation of the *Centre Gauche* (Williamson, 1885). He accepted this position in order to be able to influence scientific development. He was nominated Chevalier de la Legion d'Honneur in 1850, promoted to Officier in 1863, to Commandeur in 1869, and to Grand officier in 1881; in 1879 he was also a member of its council (Friedel, 1885). He was an active member of the Commission des Hôpitaux Civils et Militaires and of the Comité Consultatif d'Hygiene, which he presided after 1879.

### Scientific activities

The scientific contribution of Wurtz is considerable both in the experimental and theoretical fields (André, 1956). His most important achievements in these areas will now be described in some detail.

#### 1. Hypophosphorous acid

Wurtz's first significant work, started at Liebig's laboratory and completed at that of Dumas, was related to the constitution of hypophosphorus acid. Dulong's most important contribution to the chemistry of phosphorus was his discovery of a new phosphorous acid (Dulong, 1816). According to Dulong the combination of phosphorus with oxygen gave place to four different acids and he proposed that the one with the minimum amount of oxygen be named *hypo-phosphoreux* (hypophosphoric acid). Dulong prepared this acid by neutralizing the liquor that remained from the reaction between barium phosphide and water. The filtrate from the reaction was concentrated by evaporation yielding a very acid viscous liquid that could not be crystallized. Heating this acid produced phosphine, a little of phosphorus sublimed, and a remaining liquid that was essentially a phosphoric acid. Analysis of the liquid indicated that it contained 72.75 mass percent phosphorus and 27.25 mass percent oxygen, corresponding to the formula  $P_4O_3$  (on a water-free basis) for the acid and  $P_2O_3$  for the anhydride (Wurtz, 1843).

Dulong's study of the new acid was followed by a very detailed one done by Rose (Rose, 1827, 1828). The results of the two hardly agreed, Rose claiming that the actual composition by mass was 79.69% phosphorus and 20.31% oxygen, corresponding to the formula  $P_2O$  for the acid and  $PO$  for the anhydride. In addition, Rose believed that the acid could

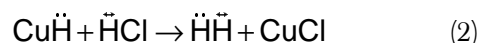
be considered as a combination of phosphoric acid and hydrogen sulphide.

According to Wurtz Rose had determined the amounts of oxide and phosphorus directly and those of water and oxygen by difference. Since there was no method available for determining phosphoric acid directly, particularly in a liquor that contained at the same time barite or calcium hydroxide, Wurtz adopted a different analytical approach: to determine the amounts of oxide and water directly, the acid by difference, and the amount of phosphorus in the barium salt. This procedure, which allowed the exact determination of the amount of water present in hypophosphites, led him to the formula  $PH_2O_2H$  for the acid and  $P_2H_4O_3$  for its anhydride, in accordance with Liebig and Humphry Davy (1778-1829), who had proposed to consider all acids as hydracids. Hypophosphorus acid was thus monoacid (Wurtz, 1843).

Wurtz then studied phosphorus acid, phosphoric acids, their esters and salts, and showed that in the three acids of phosphor the amount of hydrogen remained constant and that their acidity increased with the proportion of oxygen (Urbain, 1934):



Wurtz also studied the properties of hypophosphorous acid and found that when heated gently with sulfuric acid it was reduced, depositing sulfur and releasing sulfur dioxide. In addition he observed that hypophosphites reacted with cupric sulfate releasing hydrogen and separating copper hydride and pure copper, which deposited on the walls of the test tube as a brilliant mirror (Wurtz, 1844b). Later on he used this result as argument in favour of the diatomicity of the hydrogen molecules. Wurtz discussed the mechanism of this reaction in a manner quite similar to the present one, and retained the proposed scheme for reasons of polarity. Wurtz wrote (André, 1956)



Other hydrides were prepared afterwards. Copper hydride, whose nature was hard to determine, was used by Luigi Chiozza (1828-1889) as hydrogenating agent in the hydrogenation of acetyl chloride to acetaldehyde.

Boiling potassium hypophosphite in the pres-

ence of an excess of potassium hydroxide generated hydrogen and a more oxidized salt. With alkalis hypophosphorous acid formed salts, which were crystalline and very deliquescent. Concentrated aqueous solutions of these salts absorbed oxygen from air slowly and generated phosphorus acid. Ammonium hypophosphite crystallized easily yielding hexagonal lamina that was highly deliquescent. Calcium and lead hypophosphites were slightly soluble in cold and hot water (Wurtz, 1843).

During this work Wurtz discovered sulfophosphoric acid (prepared by the action of alkali over phosphorus chlorosulfide, a tribasic acid that may be considered a phosphoric acid in which one oxygen atom has been replaced by sulfur) and phosphorus oxychloride (prepared by the action of a small amount of water on phosphorus pentachloride), which was afterwards utilized by Gerhardt to prepare the chlorides and anhydrides of the acids. Wurtz also proved that phosphorus acid,  $\text{PO}_3\text{H}_3$ , reacted as a diacid and that in phosphorus trichloride and pentachloride two of the chlorine atoms are retained by a weaker force than the remaining ones (Wurtz, 1847b; André, 1956, Urbain, 1934).

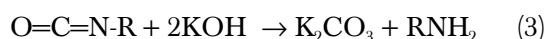
Wurtz's work on phosphorus almost cost him the vision of one eye: he tried to react sodium with phosphorus trichloride at room temperature with no success. Heating the mixture in an open test tube resulted in a violent reaction that shattered the tube. Some glass fragments hit his face and hands and left him temporarily blind. After some days his vision returned but he was left with a temporary cataract, which was later cured by a minor operation.

## 2. Ammonia derivatives

This is the subject where Wurtz made some of his most important discoveries. He showed that heating urea in the presence of chlorine transformed it into cyanuric acid (pyrouric acid, tricarbimide a trimer of cyanic acid,  $\text{C}_3\text{O}_3\text{N}_3\text{H}_3$ ), and that this compound presented a triple acid function, as Liebig thought, and was not a dibasic acid according to Wöhler (Friedel, 1885). During this work he prepared liquid cyanogen chloride (CICN) and other compounds by the dry distillation of a mixture of cyanate and sulfovinat (ethyl potassium sulfate,  $\text{C}_2\text{H}_5\text{KSO}_4$ ) or potassium sulfomethylate. These ethers were later named isocyanic esters (and later on, isocyanates  $\text{R-N=C=O}$ ), to distinguish them from the true cyanic esters (Wurtz, 1844c; 1846b; 1847a,b; 1848a,b; Friedel, 1885).

Reaction of isocyanates with ammonia and

water led to substituted ureas,<sup>2</sup> the first members of which were synthesized by Wurtz. Reaction with potassium hydroxide led to ammonia compounds, totally unknown until then (Urbain, 1934); the reaction produced potassium carbonate and a gas having ammoniacal odor that in the beginning Wurtz assumed to be ammonia. In a brilliant stroke of speculation he asked himself where did the carbon and hydrogen from the alkyl group go. Pretty soon he realized not only that the gases were combustible but also that they were also different from ammonia and that the difference depended on the original compound. In this manner he was led to the discovery of amines (Wurtz, 1849a; André, 1956):



According to André (André, 1956) here is an example of a fortuitous discovery, whose merits belong to the outstanding qualities of the researcher. Wurtz applied his penetrating spirit to its interpretation and concluded that "les combinaisons  $\text{CH}^5\text{Az}$  and  $\text{C}^2\text{H}^7\text{Az}$  peuvent être considérées comme de l'éther méthylique dans lequel l'équivalent doxygène serait remplacé par un équivalent damidogène  $\text{AzH}_2$ , ou comme de l'ammoniaque dans laquelle un équivalent d'hydrogène est remplacé par du méthylum  $\text{CH}^3$  ou de éthylum  $\text{C}^2\text{H}^5$ " (the compounds  $\text{CH}_5\text{N}$  and  $\text{C}_2\text{H}_7\text{N}$  may be considered as methyl ether in which the equivalent of oxygen has been replaced by an equivalent of amidogen  $\text{NH}_2$  or as ammonia in which the equivalent of hydrogen has been replaced by methyl  $\text{CH}_3$  or ethyl  $\text{C}_2\text{H}_5$ ) (Wurtz, 1849b).

A few months later Hofmann discovered secondary and tertiary amines thus supporting Wurtz's second point of view that not only one hydrogen can be replaced once by the methyl, ethyl, propyl, etc. radical, but the other two hydrogen atoms are equally replaceable, maintaining the type and the function (Hofmann, 1849). All these results gave a substantial support to Gerhardt's theory of types (see below) (André, 1956).

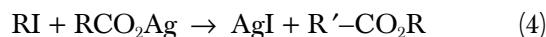
In a following work (Wurtz, 1853a,b, 1854) Wurtz studied the action of acids on alkyl isocyanates and discovered the substituted amides, presenting a double function: acid and alcohol, a result that complemented a previous discovery by Gerhardt and Chiozza about amides containing many acid groups

<sup>2</sup> Alkyl cyanates ( $\text{N=C-OR}$ ) were discovered at the same time by François Stanislaus Cloëz (1817-1883).

(Gerhardt and Chiozza, 1853; André, 1956). Wurtz applied to this series of compounds Gerhardt's views relative to acids, which considered them to be related to type water. Amides could thus be looked upon as acids in which one molecule of oxygen had been replaced by the residue AzH (NH) of ammonia which had lost two hydrogen atoms, or by this same residue containing a radical substituted at the hydrogen (Friedel, 1885).

### 3. Esterification—the Wurtz reaction

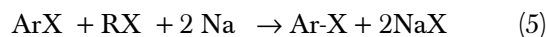
In 1854 Wurtz discovered butyl alcohol in a complex commercial product called “amyl alcool brut”, obtained as the bottom product of the distillation of the alcohol removed from the fermentation of beet molasses. Wurtz made a detailed study of this alcohol and prepared a large number of its derivatives, in particular butyl iodide because of the known reactive properties of alkyl iodides (Wurtz, 1852). Reaction of butyl iodide with silver acetate yielded butyl acetate and silver iodide:



This reaction is nowadays called “the Wurtz reaction”.

Wurtz wrote: “Je me suis assuré que généralement tous les éthers iodydriques possèdent la propriété de décomposer les sels d'argent secs et que ce procédé d'étherification pourra s'appliquer à la préparation d'un grand nombre d'éthers nouveaux ou tout au moins difficiles à préparer par les moyens ordinaires” (I am convinced that in general, all alkyl iodides are capable of decomposing dry silver salts and that this etherification process can be applied to the preparation of a large number of ethers, which are either unknown or at least hard to prepare by ordinary means) (Wurtz, 1852).

The concept of the Wurtz reaction was expanded by Rudolf Fittig (1835-1910) in the mid 1860's, who discovered that in the presence of metallic sodium, hydrocarbons could be synthesized that contained the combination of an alkyl radical (R) and an aromatic residue (Ar) (Fittig, 1864):



### 4. Radicals

In 1849-1850 Edward Frankland (1825-1899) and Hermann Kolbe (1818-1884) announced the isolation of methyl and ethyl radicals, a result that attracted much attention to the subject since it was not known if methyl, ethyl, etc., existed on the free state or associated by dimerization (Frankland, 1849;

Kolbe 1850). Dumas, who had not forgotten Amedeo Avogadro's (1776-1856) viewpoint and believed that the molecule of hydrogen should be represented as  $\text{H}_2$ , thought that the methyl and ethyl radicals of Frankland and Rose were actually their dimers, that is, ethane and butane. Later on, Hofmann gave arguments for this interpretation, but since they were based on the boiling temperatures of the new compounds, they could not convince the chemists of that time (Friedel, 1885; Urbain, 1934).

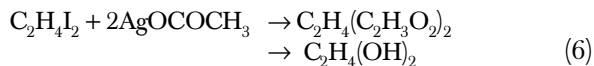
Wurtz's results on the esterification of alkyl iodides led him to the question of the existence of free radicals (André, 1956). He thought that if the radicals were actually dimers then the union of different radicals should lead to mixed hydrocarbons. Consequently he modified the above reaction (eq 4); this time he reacted a mixture of two alkyl iodides with sodium and obtained ethyl-butyl and butyl-amyl. Later on he proved that his method was general and that the mixed radicals produced had all the properties of alkanes, an observation that led to an important idea that had been expressed before: the dimerization of organic radicals represents an argument in favour of the diatomicity of the hydrogen molecules, the hydrogen atom behaves like the organic radicals methyl, ethyl, etc. (Wurtz, 1855b; André, 1956; Urbain, 1934).

### 5. Glycols

As stated by André (André, 1956), the existence and synthesis of glycols is another fundamental discovery by Wurtz, but this time it is not due to chance but to a logical reasoning. It was well known that esterification of ordinary alcohols required only one equivalent of a monobasic acid and resulted in the elimination of two equivalents of water. Berthelot had shown that glycerine, discovered by Michel Eugène Chevreul (1786-1889), combined with three equivalents of a monobasic acid and gave place to the elimination of six equivalents of water (Berthelot, 1853-1854). Wurtz combined these two findings and speculated that between glycerine and ordinary alcohols there must exist particular alcohols that esterify with two equivalents of monobasic acids and release four equivalents of water, that is, alcohols containing twice the alcoholic function. This idea, simple in appearance, was hard to put to practice. Wurtz guessed that he could realize it by applying his esterification method to the dihalogenated compounds obtained by the action of halogens on unsaturated hydrocarbons similar to ethylene. He understood that the starting point for proving his point was

in the halides of hydrocarbons similar to ethylene and thus he decided upon ethylene diiodide because of its being less stable (Friedel, 1885).

On March 1856 Wurtz prepared glycol by reacting ethylene diiodide with two equivalents of silver acetate and hydrolyzing the resulting ethylene diacetate with potassium hydroxide:



A rather violent reaction occurred and among its products was the new substance, which Wurtz had predicted as the missing link between alcohol and glycerine (Wurtz, 1856).

The problem had been solved. Afterward Wurtz modified his procedure to make it easier, replacing the iodide by the bromide, easier to prepare, and saponifying the diacetic glycol with barium hydroxide instead of potassium hydroxide (Wurtz, 1859b) (Friedel, 1885).

Wurtz's success confirmed the correctness of his ideas and the many glycols he produced served as examples of the new family of compounds (André, 1956). He wrote: "J'ai réussi à former une série de composés intermédiaires entre les alcools proprement dit et la glycérine dont les combinaisons marquent pour ainsi dire le passage entre les corps gras neutres et les éthers composés. Je nomme ces substances glycols ou alcools diatomiques; glycols pour marquer la double analogie qui les relie à la glycérine d'une part et à l'alcool de l'autre; alcools diatomiques pour exprimer ce qu'ils ont de plus fondamental dans les propriétés, c'est-à-dire un capacité de saturation double de celle de l'alcool ordinaire" (I have succeeded in forming a series of compounds intermediate between the alcohols and glycerine, where the combinations show the passage between neutral fats and esters. I name these substances glycols or diatomic alcohols; glycols to indicate the double analogy that on the one hand connects them to glycerine and, on the other, to alcohols; diatomic alcohols to point out one of their more fundamental properties, their capacity of double the saturation of ordinary alcohol) (Wurtz, 1856, 1859a). (André, 1956).

Wurtz demonstrated the structure of glycol by its oxidation to glycolic and oxalic acids, and build up the series of homologues: propyl, butyl, and amyl glycol (Wurtz, 1863). Oxidation of glycols also allowed Wurtz to show the relation between glycols and alkyl acids of the lactic type, and in the case of glycol itself, the relation to glycolic and oxalic acids. In addition, the action of hydrogen chloride on

glycol led to monochlorhydrin, from which, by the action of potassium hydroxide, he produced ethylene oxide (Wurtz, 1859b). He could now explain the nature of "the oil of the Dutch chemists" (ethylene dichloride): It was a chloride that bore the same relationship to glycol as the long-known ethyl chloride did to ethyl alcohol (Wurtz, 1856; Farber, 1956).

Reaction of Dutch oil (ethylene dichloride) with potassium hydroxide also gave ethylene oxide, a highly reactive isomer of acetaldehyde. With water, ethylene oxide formed not only glycol but also diethylene alcohol and the corresponding tri- and tetraethylene glycols. In ethylene glycol Wurtz found another link to inorganic chemistry: the polyethylenic alcohols (polyethylene glycols) were analogues to the polysilicates and polystannates (Wurtz, 1863; Farber, 1956).

Within this project Wurtz also synthesized glycerine and studied the synthesis reaction in depth (Wurtz, 1855a, 1857).

Ethylene oxide reacted with ammonia and its homologues to yield oxygenated bases. Within this project Wurtz synthesized neurine or choline (Wurtz, 1867).<sup>3</sup> Adolf Baeyer (1835-1917) had shown that the latter is an oxyethylenic base, a hydrate of oxyethylenetriammonium. Wurtz was able to obtain it by the reaction of trimethylamine and glycol monochlorhydrin and to prove that it was identical with the natural choline isolated by Mathias Eugene Oskar Liebreich (1839-1908), (Friedel, 1885).

Wurtz showed that ethylene oxide was the organic compound corresponding to the oxides of bivalent metals, contributing with these arguments to the theory of valence (André, 1956). Wurtz could not have imagined that within 50 years these two compounds, ethylene glycol and ethylene oxide, would become major chemical commodities, each manufactured to the tune of about 10<sup>7</sup> tons per year.

The study of the reactions of glycol led to a series of interesting results. Oxidation in the presence of platinum black produced glycolic acid (hydroxyacetic acid, OHCH<sub>2</sub>COOH). A more energetic oxidation produced oxalic acid, thus two important acids were found to be connected to an

<sup>3</sup> Neurine is a poisonous organic base formed in the decomposition of protagon (a nitrogenous phosphorized principle found in brain tissue) with boiling baryta water and in the putrefaction of proteinic matter. It was for a long time considered identical with choline, a crystalline body originally obtained from choline. Chemically, however, choline is oxyethyltrimethylammonium hydroxide, while neurine is trimethylvinylammonium hydroxide.



alcohol of the same atomicity. Reaction of the glycol with hydrogen chloride gave monochlorhydrin, whose decomposition by potassium hydroxide produced ethylene oxide. Wurtz extended his researches to the homologues of glycol preparing propylene glycol, butylenes glycol, amylene glycol, as well as many derivatives of the same. The controlled oxidation of propylene glycol led to lactic acid, similar to glycol producing glycolic acid (Wurtz, 1858; Friedel, 1885).

Alexander William Williamson (1824-1904) had been the first to represent sulfuric acid by the formula

$\left[ \begin{array}{c} \text{H} \\ \text{SO}^2 \\ \text{H} \end{array} \right] \text{O}^2$  in which the indivisible radical  $\text{SO}^2$  took the place of two hydrogen atoms belonging to two different water molecules and bridged these molecules one to the other. Ethylene, propylene, and other bivalent radicals played the same role in glycols (Friedel, 1885).

Wurtz believed that lactic acid, prepared routinely from propylene glycol by oxidation, was a diatomic acid. Treatment with phosphorus pentachloride yielded a diatomic chloride,  $\text{C}_3\text{H}_4\text{O}\cdot\text{Cl}_2$ , which reacted with ethanol producing chlorolactic ether,  $\text{C}_3\text{H}_4\text{OCl}\cdot\text{OC}_2\text{H}_5$ . Wurtz's hypotheses regarding the dibasic nature of lactic acid and the relations between glycols considered as diatomic alcohols and the acids of the lactic series led to a heated controversy with Kolbe. Wurtz answered Kolbe's criticism not only with arguments but also with additional experimental results. First he synthesized diethyl lactate (thus showing that lactic acid had two hydrogen atoms capable of being replaced by ethyl groups) and then substituted the second hydrogen atom with acid radicals and prepared lactobutyric acid. By comparing lactic acid with salicylic acid, and of phosphorus acid (dibasic although triatomic) to glyceric acid (monobasic could not exchange but one hydrogen atom in spite of being triatomic), he concluded: "C'est que la capacité de saturation d'un acide vis-à-vis des oxides basiques dépend non seulement du nombre d'équivalents d'hydrogène typique qu'il renferme, mais aussi de la nature électro-négative du radical oxygéné. A mesure que l'oxygène augmente dans le radical l'hydrogène typique devient de plus en plus hydrogène basique" (The saturation capacity of an acid compared to that of basic oxide depends not only of the number of hydrogen equivalents that it carries, but also of the electronegative nature of the oxygen equivalent. An increase in oxygen in the type hydrogen makes the hydrogen

more and more basic) (Wurtz, 1858; Friedel, 1885). It was left to Kolbe, eventually, to demonstrate that lactic acid was simultaneously an alcohol and an acid.

The research of lactic acid and ethylene oxide led Wurtz to the discovery of polylactic and poly thylenic compounds. Oxidation of polyethylenic alcohols produced complex acids such as diglycolic acid and diglycolethylene acid (Wurtz, 1863).

About the same time he discovered amylene hydrate (*tert*-pentyl alcohol), an isomer of amylic alcohol, obtained by reacting hydrogen iodide with amylene and decomposing the iodide formed with silver oxide and water. Wurtz named it as such as a reminder of the facility with which it decomposed under the action of heat into amylene and water. Additional work showed the hydrate to be a tertiary alcohol (Friedel, 1885).

Amylene chlorhydrate, bromhydrate, and iodhydrate provided Wurtz with interesting examples of compounds that had, so to say, two densities, one at low temperatures and another at high temperatures. Wurtz interpreted this remarkable fact by a decomposition of the molecule into amylene and hydrogen chloride, which recombined again on cooling (Wurtz, 1863; Friedel, 1885).

## 6. Atomicity and valence

Wurtz lived at a time when the known chemical doctrines were experimenting substantial improvement. At the beginning of his scientific career the theory of a vital force and the notation of equivalents was prevalent. At the end of his career the atomic theory was accepted almost universally and the structural theory of organic chemistry was established (Durand, 1968).

During the eighteenth century the vegetable and the animal subjects of chemistry were united under the subject organic chemistry. Chemistry was now composed of two branches, mineral and organic chemistry, according to the distinctive origin of compounds. To these branches were added physiological chemistry, which, in France, Wurtz converted into biological chemistry in 1874 with the creation of a specific laboratory of *chimie biologique* at the Faculty of Medicine (Carneiro, 1993).

In 1813 Berzelius had proposed a classification of matter according to behaviour in electrolysis. The two major categories were imponderable and ponderable. Imponderable included phenomena such as positive and negative electricity, light, caloric and magnetism. Ponderable bodies were first divided into simple and composite bodies and then into two

classes, electropositive and electronegative, according to whether during electrolysis they appeared at the negative or positive pole, respectively. All bodies could then be arranged in the order of their electrical nature, forming an electrochemical system that could be used to give an idea of chemistry.

Lavoisier's oxygen theory of acidity, his theory of neutral salts and his theory of organic chemistry were the immediate predecessors of Berzelius's ideas. According to Berzelius "each chemical combination should be composed of two parts united by the effect of their electrochemical reaction...each compound may be divided into two parts, of which one is electrically positive and the other negative," since only between oppositely charged elements was there attraction. Reactions occurred as the stable groups of atoms (*radicals*) were exchanged between molecules and radicals were almost as indivisible and untouchable as the individual atoms themselves (Berzelius, 1819).

To make this notion fit organic substances, Berzelius had to insist that radicals consisted of carbon and hydrogen only, with carbon negative and hydrogen positive.

Dumas was an enthusiastic supporter of Berzelius; in 1837 he and Liebig published their famous paper on the radical theory in which they boldly declared that "in mineral chemistry the radicals are simple; in organic chemistry the radicals are compound; that is all the difference. The laws of combination and reactions are otherwise the same in these two branches of science" (Dumas-Liebig, 1837).

Nevertheless, the radical hypothesis presented some difficulties in interpreting known phenomena. For example, how was it possible to explain that two hydrogen atoms could unite to become a hydrogen molecule? Attraction between two atoms required that one of them be positive and the other negative, but why should two atoms of the same kind possess charges with opposite charges? When the knowledge of organic compounds increased, new difficulties arose. Berzelius, for example, found it necessary to assume that the hydrogen atom was always positive and the chlorine atom always negative.

With increased knowledge, problems that could not be explained by Berzelius's theory became increasingly numerous and the theory became discredited. By the end of the nineteenth century it had become obvious that the only way to explain certain phenomena was to accept that there were different kinds of chemical bonds; thus the difficulties of Berzelius's theory were also explained.

In 1836, Auguste Laurent (1807-1853), a student of Dumas, realized the chlorination of ethanol (Laurent, 1836). This experiment was the fatal blow to Berzelius' views, for chlorine was considered negative and hydrogen positive, yet one could be substituted for the other without making a drastic change in the properties of a compound. Further experimentation by Laurent showed that radicals were not as indestructible and untouchable as Berzelius insisted, and that one must not overemphasize the matter of positive and negative. Eventually, the dualistic theory lost value and the new views of Laurent took over. Laurent dropped the concept of electrical forces and assumed that an organic molecule had a nucleus (which might be a single atom) to which different radicals could be attached. Organic molecules were now grouped into families or types (*theory of types*). All the members of one type would have an identical nucleus to which any of a series of similar radicals could be attached; and within the radicals there would be considerable room for variation. A particular molecular type might even extend into the realm of the inorganic.

Types came in four varieties: (a) *the hydrogen type*  $\begin{bmatrix} H \\ H \end{bmatrix}$ . Substitution of one or both hydrogen atoms by simple or composite radicals led to simple monatomic bodies, to radicals of the same atomicity, which could be isolated, and simple or composite diatomic radicals; (b) *The hydrogen chloride type*,  $\begin{bmatrix} Cl \\ H \end{bmatrix}$ . To this type belonged all the compounds formed by the combination of bromine, chlorine, iodine, and fluorine, with any monatomic radical. Although this type was redundant because it could be incorporated into the hydrogen one, it was kept for reasons of commodity; (c) *the water type*,  $\begin{bmatrix} H \\ H \end{bmatrix} \theta$ . This group included the compounds formed by oxygen, sulphur, tellurium, and selenium (marked  $\theta$ ) with different monatomic radicals, and partly, those they could form with diatomic radicals, and (d) *the ammonia type*,  $\begin{bmatrix} H \\ H \\ H \end{bmatrix} N$ . To this group belonged ammonia derivatives or the compounds in which the nitrogen of ammonia had been replaced by phosphorus, arsenic, antimony, or bismuth.

Since the above types could not help representing certain compounds which contained polyatomic radicals, Gerhardt created the simple and mixed *condensed types*, which were actually composed of the above four basic types duplicated, tripled, etc.,

for example, condensed hydrogen,  $\left[ \begin{smallmatrix} H^n \\ H^n \end{smallmatrix} \right]_0$ , condensed hydrogen chloride,  $\left[ \begin{smallmatrix} Cl^n \\ H^n \end{smallmatrix} \right]$ , condensed water,  $\left[ \begin{smallmatrix} H^n \\ H^n \end{smallmatrix} \right]_O^n$ , and condensed ammonia,  $\left[ \begin{smallmatrix} H^n \\ H^n \\ H^n \end{smallmatrix} \right]_N^n$ .

The new impulse given to the theory of types by the discovery of primary, secondary, and tertiary amines was strongly reinforced by Williamson's discovery in 1851 of the synthesis of ethers, which allowed proving the existence of mixed ethers, R-O-R'. According to Williamson "alcohol is therefore water in which half the hydrogen is replaced by carburetted hydrogen, and ether is water in which both atoms of hydrogen are replaced by carburetted hydrogen" (Williamson, 1851). Ethers could thus be built about the water type. Inherent in Williamson's proposal was that water is H<sub>2</sub>O and not O H, as had been maintained by many of his contemporaries, and that alcohol is not hydrated ether from which water has been removed by the action of the acid.

Wurtz had no hesitation in aligning himself with Laurent and Gerhardt; he was the first teacher in France to champion their ideas, and became the architect of a new chemical system that embraced their antidualist concepts as well as the emerging concepts of atomicity (valence) and chemical types. His new ideas were clearly expressed in the address *Sur l'Oxide d'Éthylene Considéré Comme un Lien entre la Chimie Organique et la Chimie Minérale* (Wurtz, 1862) he gave in 1862 to the Chemical Society. In this talk he described a new series of analogies designed to show how diethyl ether could be envisaged as an analogue of the oxide of monatomic silver, how ethylene oxide was analogous to the oxide of diatomic barium, and how glyceryl oxide was analogous to the oxide of triatomic antimony (Williamson, 1885).

One of Wurtz's most popular works was *La Théorie Atomique* (1879); its central subject was the idea of combining power or atomicity of the atoms, a new concept for which Wurtz had helped to clear the ground. Its application to the elements led inexorably to the notion of valence, credit for which belongs to several of Wurtz's contemporaries as well as to him.

The theory of types gained in popularity because it could be used to organize the rapidly proliferating numbers of organic compounds being studied. Beilstein published a vast compendium of organic compounds in 1880, and utilized Laurent's theory of

types to organize those compounds into a rational order. The type concept became more general with the synthesis of many new organometallic compounds by Frankland. Now it became clear that each metallic atom would attach to itself only so many organic groupings, and that this number was different for different metals. In 1852, Frankland proposed what later would become the theory of valence (from a Latin word for "power"), which is the statement that each atom has a fixed combining power. In addition to its basic concepts, this theory helped to clarify the difference between atomic weight and equivalent weight of an element, as well between valence and oxidation number (Frankland, 1852). By 1900, the description of molecular structure in three dimensions had become universally accepted.

Earlier, in 1848, Wurtz had studied amines. He showed they belonged to a type with a nitrogen nucleus. In ammonia a nitrogen atom was bound to three hydrogen atoms, in amines organic radicals replaced one or more of these hydrogen atoms. By dehydrating glycol, Wurtz procured ethylene oxide, a missing link that permitted him to construct a comprehensive series of analogies between organic and inorganic oxides that was based on the twin concepts of atomicity and type. Ethylene oxide was hailed as an analogue of the oxides of diatomic calcium and barium, just as glyceryl oxide could be represented as an analogue of the oxides of triatomic antimony and bismuth. On the basis of such analogical argument Wurtz proclaimed the unification of chemistry (Wurtz, 1862).

With the aid of many similar series Wurtz was able to consolidate the unification of chemistry: radicals both simple and complex could be mono, di, or triatomic (Brooke, 1971).

### 7. Miscellaneous

Other Wurtz's works are related to the preparation of an hydrate of amylene (pentene), later to be shown to be a tertiary alcohol, and a synthesis of phenol from benzene through the reaction with sulfonic acid, that led to the discovery of aldolization and crotonization. Wurtz discovered that an aldehyde in the presence of hydrogen chloride gave a condensed product that was at the same time alcohol and aldehyde (Wurtz, 1872, 1873, 1881). Wurtz found that under prolonged contact a mixture of aldehyde and hydrogen chloride gave place to a new compound, a polymer of aldehyde that presented both the functions of aldehyde and alcohol. This was an aldol, CH<sub>3</sub>CHOHCH<sub>2</sub>CHO, susceptible of transforming

into crotonic aldehyde  $\text{CH}_3\text{CH}=\text{CHCHO}$ , by loss of water. Isolation of the product showed it to be the aldol  $\text{CH}_3\text{-CHOH-CH}_2\text{-CHO}$ . Dehydration of the aldol gave a common aldehyde, crotonic aldehyde, that was easy to produce if the aldolization reaction was carried under more severe conditions (André, 1956). Wurtz proved the double functionality of aldol by performing a series of typical reactions. For example, aldol gave ethers like alcohols, it transformed into  $\beta$ -oxybutyric acid by simple oxidation, fixing one atom of oxygen as aldehydes did; hydrogenation produced butyl glycol; it combined with ammonia and the product of this reaction, when heated in a stream of ammonia, yielded collidine ( $\text{C}_8\text{H}_{11}\text{N}$ ). Distillation of aldol a resinous residue separated, from which it was possible to separate dialdane, formed by the condensation of two molecules of aldol with elimination of one water molecule. Dialdane was also an aldehyde, it yielded oxaldanic acid, a dialdanic alcohol, a base formed by the condensation of molecules of dialdane and two molecules of ammonia, with elimination of three molecules of water. The later had the interesting property that its aqueous solution coagulated on heating like albumin, but the coagulate dissolved again on cooling (Wurtz, 1873, 1881; Friedel, 1885). This discovery showed the importance and generality of the reaction that created a new carbon-to-carbon bond and allowed the elongation of the chain. ▀

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