

Charles Friedel

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ABSTRACT

Charles Friedel (1832-1899) was one of the most famous French chemists of the second-half of the nineteenth century. He conducted important research in mineralogy, in the chemistry of silicon, and in pyroelectricity. Together with James Mason Crafts he discovered the reaction that carries their names and that constitutes a powerful and versatile tool for the synthesis of an enormous number of chemicals of significant industrial value.

KEYWORDS: Friedel-Crafts reaction, mineralogy, pyroelectricity, silicon chemistry, organic synthesis, secondary alcohols

Resumen

Charles Friedel (1832-1899) fue uno de los más famosos químicos franceses de la segunda mitad del siglo diecinueve. Realizó importantes investigaciones en mineralogía, en química de los compuestos del silicio y en el fenómeno de la piroelectricidad. Junto con James Mason Crafts descubrió la reacción que lleva sus nombres y que constituye una poderosa y versátil herramienta para sintetizar una enorme variedad de compuestos de importante valor industrial.

Life and career

Charles Friedel was born at Strasbourg on March 12, 1832, the son of Charles Friedel, a banker, extremely interested in science, which had followed the popular courses on theoretical and applied chemistry organized by city of Strasbourg, and Virginie Duvernoy, the daughter of Georges Duvernoy, a famous zoologist, who became Dean of the Strasbourg Faculty of Science, and professor at the Collège de France, replacing Georges Cuvier (1769-1832), and at the Muséum d'Historie Naturelle in Paris. The scientific interest on the part of the father may have been, along with other reasons, the basis of the strong attraction that experimental sciences exercised on Charles Friedel (Béhal, 1932; Willemart, 1949).

Charles did his first studies at the Gymnase Protestant of Strasbourg where he showed that he had a keen mind; he was a serious student with good general aptitudes, and as a result his parents allowed him to fit up a room at home as a chemistry laboratory and to keep his collection of minerals and rocks there (Béhal, 1932).

The Gymnase Protestant was an institution controlled by the Lutheran Augsburg Confession. According to Carneiro (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, Friedel benefited from a bilingual education, which provided access to both French and German cultures (Wisniak, 2005).

After graduation Charles entered the Faculté des Sciences of the University of Strasbourg where Pasteur taught chemistry and was doing his research on crystallography. After receiving his bachelor's degree in letters in 1849 and in science in 1850, he worked for a year at his father's bank and while there he had the opportunity of attending lectures by Louis Pasteur (1822-1895), Auguste Daubrée (1814-1896), Pierre Auguste Bertin (1818-1884), and Dominique Auguste Lereboullet (1804-1865) at the University of Strasbourg. His father soon saw that this activity did not satisfy his son's abilities and on 1851 allowed him to go to Paris to continue his studies. In Paris, Charles, only 20 years old, lived with his maternal grandfather Duvernoy in the apartment formerly occupied by Buffon at the Natural History Museum. He received his *license de mathématique* in 1854 and his *license de sciences physiques* in 1855. Simultaneous with his university studies he began research activities at the Muséum; already in a letter, dated December 21st, 1854, Friedel speaks of the discovery of two new faces in crystals of corundum, given him for examination by the mineralogist Pierre Armand Petit Dufrénoy (1792-1857). In 1854, in spite of his work with Dufrénoy, he declined his offer for a position as assistant of mineralogy and instead, went to work in Charles-Adolph Würtz's (1817-1884) laboratory. While at the latter, Friedel followed the lectures of Henri Hureau de Sénarmont (1808-1862) at the École des Mines, and formed a strong personal attachment to him while engaged in mineralogical studies under his guidance (Béhal, 1932; Willemart, 1949).

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On November 10th, 1854, Friedel entered Würtz's laboratory and soon became his most distinguished pupil, among the sixteen young researchers pursuing scientific careers at what was considered one of the most respectable research centers in Europe (Crafts, 1900).

Friedel's friendship with Würtz was a very important factor in his career. Both were Alsations, born in Strasbourg, and graduates of the same school (Gymnase Protestant), united by similar tastes, opinions, and pursuits. Association with the senior chemist opened the doors for Friedel in professional and editorial work (Crafts, 1900).

For many years the activity of Charles Friedel was divided between the École des Mines and Würtz's laboratory. He was at first attracted by the crystallographic side of mineralogy and then towards optics, until, at the suggestion of Sénarmont, he thought of devoting himself to mathematics and becoming an astronomer; but soon the chemical side absorbed his attention, and during the remainder of his life his time was divided between pure chemistry and chemical mineralogy. Many of his publications involving new organic compounds contain a crystallographic description of the same (Willemart, 1949). During this period came the first studies on the ketones and aldehydes, lactic acid, the organic compounds of silicon (see for example, Friedel and Crafts, 1863, 1865; Friedel and Ladenburg, 1867ab, 1870; Lacroix, 1932), as well as the investigations on a hemitropic diamond crystal (Friedel, 1844-1847) and two crystals of zircon bases (Friedel, 1856), the pyroelectricity of certain minerals, the dimorphism of zinc sulfide, adamine, etc. (Friedel, 1860, 1861, 1866). In his studies about the chemistry of silicon compounds, he determined the atomic weight of the element as 28 (today, 28.06) (Friedel and Crafts, 1863) and the remarkable analogy between silicon and carbon (Friedel and Ladenburg, 1867a). Friedel and his collaborators synthesized a large number of derivatives in which the silicon atom plays the same role as that of the carbon atom, for example, tetramethyl and tetraethyl silane (Friedel and Crafts, 1863), mercaptotrichlorosilane (Friedel and Ladenburg, 1867b), hexachloro-, hexabromo, and hexaiodosilicon (Friedel, 1871), etc. In a summary of these activities they wrote: "The discovery of silicon hexaiodide proves that silicon, like carbon can partially saturate itself and thus serve to construct complicated molecular structures, the same like the organic element."

In 1856, Friedel was appointed Curator of the mineralogical collection of the École des Mines, then under the direction of Dufrenoy, a position he kept for the rest of his life. Somewhat later, Pasteur suggested that he postulate for membership in the mineralogy section of the Institut, but Friedel preferred to wait longer and enter the chemistry section, where he thought he could play a more important role. This wish crystallized in 1878 when he was elected to replace Victor Regnault (1810-1878) in that section, a position Friedel retained for the next 21 years (Béhal, 1932; Crafts, 1900). As usual for a candidate, Friedel prepared a booklet describing more than 100 of his publications in the areas of aldehydes and

ketones, organic acids, chemical combinations of silicon and titanium, mineralogy, crystallography, and crystallophysics (Friedel, 1876).

Shortly after the death of his grandfather, Friedel married at Mulhouse, on December 29, 1856, Emilie Koechlin, the daughter of an important industrialist. They had five children: Jeanne, Marie, who died very young, Marguerite, Georges, and Lucie. In 1870, at the outbreak of the Franco-Prussian War he sent his wife and children to Vernex, Switzerland, for safety, and put his chemistry knowledge to the service of the government, helping in the national defense, and serving in the National Guard (Béhal, 1932). Only after the siege and capitulation of Paris, did he learn of the death of his wife, in Montreux, Switzerland, on January 19, 1871. Two years later, on April 7th, 1873, Friedel married in Paris Louise Combes the daughter of the Director of the École des Mines. They had one son, Jean, who became maître de conférences in Botany at the Faculté de Nancy (Béhal, 1932; Willemart, 1949).

In 1861 James Mason Crafts (1839-1917), a 22-year old mining engineer from Boston joined Würtz's laboratory. Crafts had previously studied at Freiberg in Saxony and at Heidelberg. The first of their joint studies on the organic compounds of silicon was carried out during this period (1863-1865) (Friedel and Crafts, 1863, 1865). Later on (1874-1891), when Crafts returned to Paris for a second stay, a large number of papers on the famous Friedel-Crafts reaction linked their names for posterity. They were very close friends and in the Friedel memorial Lecture, given to the London Chemical Society in 1900, Crafts said: "During thirty-eight years in which a close friendship made him a witness of conduct and actions, the writer cannot recall a single instance in which he would have wished his friend to have thought or acted otherwise than he did" (Willemart, 1949).

In 1869 Friedel defended at the Sorbonne his two doctoral theses, one in organic chemistry, *Recherches sur les acetones et les aldehydes*, and the other on mineralogy, *Sur la pyroelectricité dans les cristaux conducteurs de l'électricité*.

In 1871 Friedel was put in charge of the chair at the École Normale Supérieure, replacing Alfred Des Cloizeaux (1817-1897). In 1876, he was appointed Professor of Mineralogy at the Sorbonne succeeding Gabriel Delafosse (1796-1878) and there he organized a laboratory for mineralogy. He held the Sorbonne chair until 1884, when he succeeded Würtz as professor of organic chemistry and director of the research laboratory at the Sorbonne. The death of Würtz in 1884 left Friedel as the oldest representative of Würtz's school (Béhal, 1932; Willemart, 1949).



During all his life Friedel conducted research in mineralogy. As curator of the collections at the École des Mines he had opportunities to discover new species, which he named in honor of his friends, e.g. würtzite, delafossite, carnotite, and adamine. He spent considerable effort trying to produce minerals artificially, since he was especially interested in clarifying the geologic conditions that prevailed during their formation. In addition, he was particularly attracted by the phenomenon of pyroelectricity (Willemart, 1949).

For a long time, the laboratory accommodation for chemical students at the Sorbonne and other places was very insufficient at Paris and a project for new and greatly enlarged buildings was under consideration. Würtz worked hard to improve this situation through his influence in Government circles; unfortunately he did not live long enough to see the fruits of his efforts. Shortly before his death orders were given for the construction of a large modern laboratory at the Sorbonne, the plans of which were matured and the construction superintended by Friedel. Afterwards Friedel was able to obtain the creation of the École de Chimie. In January 1895 the laboratories were opened with places for thirty students in organic chemistry, and at the same time Friedel organized a three-year course of lectures and laboratory instruction in industrial chemistry at the provisional laboratories (Béhal, 1932; Crafts, 1900).

Friedel suffered for many years of ulcers; in 1899 his illness took a turn to worse; a situation that was aggravated by the death of his nephew Edmond Alphonse Combes (1858-1896), which worked with him. He was forced to take a vacation at Montauban at the house of his son-in-law, Henri Bois, professor of Systematic Theology, at Montauban. There he passed away on April 20 (Béhal, 1932; Crafts, 1900).

The terms of the Treaty of Frankfurt, ending the French-German war, incorporated Alsace and parts of Lorraine to Germany; the loss of his homeland caused Friedel much grief awakened in him the need to participate in the effort to recover the national pride. Friedel soon began to worry seriously about the phenomenal progress of the German chemical industry. In Friedel's opinion, the lack of qualified chemists and competent technical men was one of the main reasons for the inferiority of the French chemical industry. Accordingly, from 1892 he strongly advocated the establishment of a school for the training of technical chemists. These efforts led to the founding of the Institut de Chimie (Willemart, 1949).

Honors and awards

Friedel received many honors for his contributions to science and public life. He was honorary, correspondent, or associate member of the most important European scientific societies. The Royal Society awarded him the 1880 Davy medal, Oxford University awarded him the D. C. L. in 1894. He was appointed officer of the Legion d'Honneur in 1885 (promoted to Officier in 1888), and commander of the orders of Saint-James (Portugal) and of the Romanian Crown. Together with Würtz, Adolphe Perrot (1833-1877) and others, they

founded the Société Chimique (1857) in which Friedel served four times as its president. He was also one of the founders and presidents of the Société Minéralogique de France, and took the chief part in 1899 in founding, with George F. Daubert the *Revue Générale du Chimie Pure et Appliquée*, which is largely devoted to industrial applications. In 1882 he was elected President of the Association Française Pour l'Avancement des Science. The Congrès International de Chimie appointed a committee for studying the reform of chemical nomenclature. Friedel was elected its president at the April 1892 meeting in Geneva, where the fundamental laws applicable to the acyclic series were agreed on. Friedel also presided at the International Congress of Chemists held in 1892 at Geneva for the reform of the nomenclature of the fatty acid series. Friedel was associated with Würtz in editing the *Dictionnaire de Chimie Pure et Appliquée* (Würtz, 1868-1878) and after Würtz death in 1884 he became the chief editor of the supplements (Béhal, 1932; Crafts, 1900; Willemart, 1949).

Scientific contribution

Friedel's chemical research was extremely varied and was carried out in widely different fields. Here we will describe the ones related to his two doctoral theses.

Pyroelectricity

The pyroelectric effect, where a material generates an electric charge in response to a temperature change, was studied by Carl von Linné (1707-1778) and Franz Maria Ulrich Theodosius Aepinus (1724-1802) in the mid-18th century. Drawing on this knowledge, both René Just René Just Haüy (1743-1822) and Antoine Henri Becquerel (1852-1908: 1903 Nobel Prize for Physics) showed that there was a clear relationship between mechanical stress and electric charge; however, experiments by both proved inconclusive.

At the time when Friedel began his mineralogical work, the pyroelectric phenomena observed in crystals did not appear to be always in accord with the ideas of symmetry and homogeneity of the crystalline form, which had developed by geometrical and optical studies. Of the two theses doctoral defended by him in 1869, one was on pyroelectric phenomena in crystals.

In a note published in 1857, Marbach (Marbach, 1857) explained that the unusual crystallographic characteristics of iron sulfide (FeS_2 , cubic pyrite) and gray cobalt ($\text{CoS}_2 + \text{CoAs}_2$) had led him to study their physical properties. Marbach found that crystals of FeS_2 of the same chemical quality and shape could be divided into two classes exhibiting opposite thermoelectric properties; with two fragments of pyrite, properly selected, it was possible to build a thermoelectric couple having an electromotive power larger than one made of bismuth-antimony. In addition, the negative variety was more negative than bismuth and the positive one, more positive than antimony. Friedel repeated Marbach's experiments with the intent of finding a relation between the electrical properties

and the crystalline form of pyrite and verified that the two varieties of different thermometric sign were sometimes present in the *same* crystal. Touching the pyrite with a hot and a cold wire of platinum (or iron) produced a positive or negative current, depending on the variety being tested. A close examination of the faces of cubical pyrite obtained from the mine of Traverselle showed that it was not homogeneous; certain parts were smooth while others presented grooves of a given geometrical orientation. Both kinds of areas had opposite thermometric signs. These particularities were due of the existence of dark spots; part of the structure reminded that of quartz crystals, formed by a mixture of right and left crystals (Friedel, 1869b).

Subsequent investigations were made in collaboration with Pierre Curie (1859-1906, Nobel Prize in Physics) and his brother Jacques Curie (1856-1946), and with Arnaud de Grammont (1861-1923). In a series of papers published with Jacques Curie (Friedel and Curie, 1883ab, 1885) Friedel showed that when a hexagonal crystal having three horizontal axis of hemimorphism (such as in quartz) is heated homogeneously, there is a compensation of the effects produced by the three pyroelectric compensate one another and no poles of opposite sign manifest themselves. If the heating is done on a plane normal to one of the pyroelectric axis, then lateral pressures are produced that result in a generation of positive electricity on one face and negative on the other one. These observations were particularly interesting because François Ernest Mallard (1833-1894) had shown, with the help of optical properties, that boracite was not actually cubic, it was formed of twelve orthorhombic pyramids having their vertices at the center of the solid and possessing hemimorphism axes parallel to the small diagonals of the basis of the pyramids. Mallard had also found that boracite becomes really cubic at about 265°C, and remains so up to its fusion temperature. Friedel and Curie (Friedel and Curie, 1883b) proved that boracite was pyroelectric up to 265°C and not pyroelectric at higher temperatures. Not only that, on heating a crystal a high temperature, at 265°C a sudden discharge of electricity took place. The phenomenon was due to a molecular transformation of boracite, orthorhombic with complex macles below 265°C, and cubic above 265°C; its intimate structure was thus related with the external symmetry that was cubic and tetrahedral.

Friedel showed that a crystal of topaz had a pyroelectric axis parallel to the axis of the prism (Friedel, 1879), a result that contradicted the claim of Riess and Rose that the axis was not vertical, but horizontal. Friedel and Jacques Curie decided to investigate these results again (Friedel and Curie, 1883ab, 1885ab) and designed a new piece of equipment that eliminated most of the possible sources of errors. Instead of heating the crystal itself and then applying an electrometer at different times and different locations during the cooling process, they placed a small heated (to about 100°C) hemisphere connected to an electrometer on the cold surface of a raw crystal or cut in sheets perpendicular to the known pyroelec-

tric axis. By this procedure, the two extremes of the crystal acquired a different charge. The measurements showed that quartz was pyroelectric in the three directions parallel to the axis joining the mid-points of the two opposite edges of the hexagonal prism. Through such an experiment, they became the first to recognize the difference between uniform and non-uniform heating. Friedel and Curie showed that no pyroelectric phenomena take place in crystals of the tertiary system of hexagonal crystals (like quartz), which have three axes of hemimorphism on the same plane. They also proved that a crystal of topaz is composed of four clinorhombic crystals, grouped around a central orthorhombic crystal (Friedel and Curie, 1885b).

The speculation that these observations may have been due to pressures resulting from non-uniform heating led Jacques and Pierre Curie to their discovery of piezoelectricity in 1880 (Curie and Curie, 1880), which they announced it in the following words: "We have found a new way to develop electric polarization in crystals of this sort, which consists in subjecting them to different pressures along their hemihedral axes. The effects produced are analogous to those caused by heat."

Organic chemistry

1. Aldehydes and ketones

Gustav Charles Bonaventure Chancel (1822-1890) and Charles-Frédéric Gerhardt (1816-1856) were the first to consider ketones (then called *acetones*) as compounds homologues to aldehydes, that it, as aldehydes where a hydrogen atom had been replaced by an alcohol radical (Gerhardt and Chancel, 1851). Alexander Williamson (1824-1904) experiments had later supported this point of view: distilling a mixture of potassium acetate and potassium valerate yielded an acetone intermediate with those in the original mixture (Williamson, 1850). Friedel proved that what Williamson had done for the fatty acid series could also be extended to that of the aromatic acids (Friedel, 1857). He first distilled an intimate mixture of calcium acetate and benzoate and obtained a mixture of equivalent weights of acetic and benzoic acids. Fractional distillation of the latter produced a clear, almost colorless liquid, having a pleasant odor very similar to that of bitter almond essence, boiling at 198°C and depositing at 14°C large crystalline lamina, having a composition $C_{16}H_8O_2$. The liquid was very similar to benzoyl hydride (benzaldehyde), which could be considered as derived by substitution of the hydrogen atom in the aldehyde group by a methyl one. In Friedel's word, the product was really a mixed radical, "un methylure de benzoïle comme l'acétone ordinaire est un methylure d'acétyle" In the same way he obtained methyl butyl ketone by distillation of a mixture of calcium acetate and butyrate (Friedel, 1857).

Afterwards, Friedel developed an alternative procedure for preparing mixed acetones (Friedel, 1858). While distilling calcium butyrate to prepare propyl butyl ketone (butyrene),

he observed the simultaneous production of a small amount of butyral, two compounds that are mixed ketones. This result was easy to understand because the decomposition of calcium butyrate took place with release of methane. Friedel concluded that the experimental facts showed that the distillation of a salt of the fatty acid series produced, in addition to the ketone and the hydride of the acid radical, mixed acetones containing the radical of the acid combined with the hydrocarbon radical C_nH_{n+1} , lower than that contained in the ketone. This result allowed understanding why acids with a large equivalent hardly produced substantial quantities of their ketones (Friedel, 1858).

Friedel electrolyzed an aqueous solution of acetone acidified with sulfuric acid and after some time noticed that the smell of acetone had been replaced by that of acetic acid (Friedel, 1859). Analysis of the solution with silver nitrate and litharge showed the presence of formic and acetic acids. The gas liberated at the poles of the pile was found to be an explosive mixture of hydrogen diluted with carbon dioxide. These results showed that the nascent oxygen produced in the pile oxidized acetone to acetic acid, formic acid, carbon dioxide, and water. Carbon dioxide originated from the total oxidation of a small amount of acetone. Friedel's results showed that the acetic acid was not the result of a secondary oxidative action on acetic acid formed first. Additional experiments led Friedel to conclude that the formic acid definitely originated from the oxidation of the methyl group present in acetone (Friedel, 1859).

In 1862 Würtz reported that he had succeeded in hydrogenating ethylene oxide to ethanol using nascent hydrogen produced by the sodium amalgam, but had failed in converting the isomer, acetaldehyde, into the alcohol using the hydrogen produced by the action of sulfuric acid or hydrogen chloride on zinc, iron, or an amalgam of zinc (Würtz, 1862a). In a following paper he reported that the hydrogenation was only partially possible when using sodium amalgam because the resulting sodium hydroxide resinified part of the aldehyde (Würtz, 1862b). Friedel extended Würtz' research and succeeded in reducing benzaldehyde to benzilic alcohol with sodium amalgam (Friedel 1862). The process was not feasible with zinc and acid because benzaldehyde presented the curious property of arresting the dissolution of the metal in the acid. Although the metal was covered with large hydrogen bubbles, these disengaged extremely slowly. Similarly, valeraldehyde was reduced to amyl alcohol and acetone to a propyl alcohol, which was not identical with the primary one (b.p. 97.31°C) discovered by Chancel in 1853 among fermentation products (Chancel, 1853), because by oxidation it regenerated acetone. Friedel believed that his alcohol was identical with the propyl alcohol prepared by Marcelin Berthelot (1827-1907) in 1855 by the action of sulfuric acid on propylene (Berthelot, 1855). Friedel declared that the latter should be considered as a representative of a new class of alcohols, namely, the secondary alcohols. He would later call this alcohol, isopropanol (Friedel and Silva, 1873b). Hermann

Kolbe (1818-1884) had predicted their existence shortly before on purely theoretical grounds (Friedel, 1862). Friedel found that the hydrogenation of acetone by means of sodium amalgam produced an additional compound, pinacone, which on treatment with acid changed into pinacoline (2,3-dimethyl-2-butanone). He proved that pinacone is a product of double reduction (of two keto groups), making it the first known example of a bi-tertiary glycol (Willemart, 1949). Later, in 1873, Friedel and Silva described a process for the convenient preparation of large quantities of pinacone (Friedel and Silva, 1873e). Afterwards, Friedel and Silva studied the action of nascent hydrogen on pinacoline (Friedel and Silva, 1873b) and found that the sodium amalgam reduced easily the compound to a tertiary alcohol, which they named pinacolic alcohol; this alcohol, isomeric with the known hexanols, had a pungent taste, smelled like camphor, was very soluble in water, and boiled at 120.5°C. Oxidized with a solution of dilute sulfuric acid and potassium dichromate it regenerated picoline.

Friedel also studied the products of the action of phosphorus pentachloride on the ketones, obtaining a new propylene dichloride and monochloro propylene. The chief purpose of this work was to furnish further proofs of a similarity of function between aldehydes and ketones. Auguste Cahours (1813-1891) had shown that an aldehyde treated with phosphorus pentachloride does not break up like an alcohol or ether, but that two atoms of chlorine are substituted for oxygen (Cahours, 1847). Friedel completed the demonstration by showing that acetone behaved in the same way (Crafts, 1900).

Friedel and Silva prepared propylene from acetone and then, treating it with chlorine and iodine monochloride, converted it in to trichlorohydrin and glycerol (Friedel and Silva, 1871ab, 1872ab, 1873ad).

2. Lactic acid

Würtz and Friedel (Würtz and Friedel, 1861) analyzed the difference between the two characteristic hydrogen atoms present in lactic acid, $CH_3-CHOH-COOH$. The one on the acid group was strongly basic, it was replaced easily by a metal or an organic group like ethyl; yielding in both cases a neutral compound, a metallic or ethyl lactate. Oxygenated groups such as monobasic acid radicals could easily replace the hydrogen atom in the hydroxyl radical. When replaced by an indifferent group, such as ethyl, the resultant material was acid. Lactic acid was clearly an intermediate between propyl glycol and malonic acid, as glycollic acid is intermediate between glycol and oxalic acid. Also, the properties of the material resultant from exchanging one or the other hydrogen atom would completely different. Würtz and Friedel prepared several derivatives of lactic acid and studied their properties; among them, we can mention lactic acid anhydride, lactamide, lactylethylamide, polylactic compounds such as dilactic and trilactic ethers, and lactosuccinic ether. Friedel and M. V. Machuca worked out a new synthesis of this acid,

which consisted on brominating propionic acid and then treating the product with moist silver oxide. By this procedure they also converted butyric acid into the corresponding hydroxyacid, dibromobutyric acid into glyceric acid, and butalanine by the action of ammonia on bromobutyric acid (Friedel and Machuca, 1861ab, 1862).

3. The Friedel-Crafts reaction

In 1877, Friedel and Crafts published three short notes (Friedel and Crafts, 1877abc) describing their study of the action of metallic aluminum, as fillings or slim leaves, on different organic chlorides. The reaction, which took place only with heating, occurred at first very slowly and then rapidly became tumultuous and could not be controlled even by cooling. Addition of a very small amount of iodine led to an immediate reaction, with abundant release of hydrogen chloride, and in the case of certain chlorides like amyl chloride, hydrocarbon gas was also released and numerous liquid hydrocarbons formed, which boiled at very high temperature. These surprising results led them to investigate if the reaction was due to a metallic chloride, instead of to the presence of a metal. Addition of small amounts of anhydrous aluminum chloride to amyl chloride, under cold conditions, led to a very live reaction with the simultaneous release of a gas composed of hydrogen chloride and saturated hydrocarbons. On the basis of these results Friedel and Crafts speculated that organic chlorides were attacked by aluminum chloride with loss of hydrogen chloride and that the products contained a large proportion of saturated hydrocarbons produced by the *polymerization* of amylene. The reaction seemed to offer a general synthesis procedure for preparing an unlimited number of hydrocarbons and oxygenated compounds. Reaction of an hydrocarbon with an organic chloride in the presence of aluminum chloride would lead to the combination of the hydrocarbon radical of the organic chloride with the other hydrocarbon, deprived of a hydrogen atom.

Friedel and Crafts proved their hypothesis to be true: mixing amyl chloride with an excess of benzene in the presence of a very small amount of aluminum chloride led to the synthesis of amyl benzene. They also verified that the same reaction took place with alkyl iodides and bromides, with toluene and other methyl and alkyl derivatives of benzene, and with aluminum iodide and bromide. Tetraphenyl methane (unknown at that time) was easily prepared reacting carbon tetrachloride with benzene, benzophenone by the reaction of benzoyl chloride with benzene, phthalophenone by the reaction of phthaloyl chloride with benzene, etc., etc.

In their third note (Friedel and Crafts, 1877c), Friedel and Crafts reported that other metallic chlorides (such as zinc chloride, ferrous and ferric chloride) could also be used to perform alkylations, but were less effective. The note ended giving a possible explanation of the reaction based upon the formation of a very small amount of an organometallic compound of the phenyl radical with aluminum chloride, $C_6H_5 \cdot Al_2Cl_5$ which, which reacted with the organic chloride

generating the new hydrocarbon and regenerating the aluminum chloride, according to the equation $C_6H_5 \cdot Al_2Cl_5 + RCl = C_6H_5R + Al_2Cl_6$. In a much later paper, devoted to addition reactions, Friedel and Crafts corrected their interpretation of the mechanism of the reaction and indicated that aluminum chloride participated in the reaction without the possibility of being regenerated, and thus should be always used in an amount appropriate to those of the products to be formed. The latter restriction was not required for the fixation of unsaturated hydrocarbons on benzene and other aromatic hydrocarbons. Here there was not release of hydrogen chloride and stoichiometric amounts of aluminum chloride were not required (Friedel and Crafts, 1888a)

In a preliminary memoir (Friedel and Crafts, 1874), Friedel and Crafts described their efforts to transform amyl chloride into the corresponding iodide, according to Gavriil Gustavson's method, consisting in reacting the organic chloride with aluminium iodide (Gustavson, 1874), but instead of using the latter previously prepared, they added to the chloride the required amounts of iodine and aluminium, to prepare aluminium iodide. A live reaction took place that did not produce the required iodide. They found that the iodine could be suppressed and observed the release of hydrogen chloride of the order of magnitude of the total elimination of the chlorine from the organic compound, and they got the idea that operating in the presence of a cyclic hydrocarbon with aluminium chloride, the halogenated fatty derivative could provide the halogen and the cyclic hydrogenated carbide with formation off a mixed carbide, for which Zincke had provided example employing zinc powder but without explaining the mechanism (Béhal, 1932).

As quoted by Willemart (Willemart, 1949) Hanriot described the circumstances that led to the discovery of the Friedel-Crafts reaction as follows: "About 1873, a foreign student whose name I have forgotten was carrying out a preparation in Würtz laboratory by means of Zincke's method (action of zinc dust on a mixture of chloride and an aromatic hydrocarbon). The reaction rapidly became tumultuous and Friedel, who happened to be present, helped the young gentleman to separate the liquid from the powdered zinc. To the astonishment of him and all the onlookers, the decanted liquid reacted just as vigorously as when it was still over the zinc dust. This singular cue was discussed for a while in the laboratory circle, but it was then forgotten. Some time later, Friedel and Crafts wished to convert an organic chloride into the iodide by Gustavson's method, which consists in putting the chloride in contact with aluminum iodide. They tried to modify the procedure by using a mixture of equivalent quantities of aluminum and iodine in place of the iodide. These conditions resulted in an extremely vigorous reaction, which did not produce the desired iodide. They soon discovered that the reaction goes on just the same if the iodine is omitted, that it grows faster and faster, becoming violent and cannot be controlled by cooling and by removing the strips of aluminum. At the same time, they found that a considerable part of the

aluminum is present as chloride in the liquid and they became convinced that the addition of aluminum chloride directly to the organic chloride gives the same results as metallic aluminum. The analogy to the Zincke reaction became plain and Friedel and Crafts obtained amyl benzene through the action of aluminum chloride. The reaction proceeds so regularly that the quantity of hydrochloric acid can be used to measure the amount of amyl benzene formed" (Willemart, 1949). Friedel and Crafts reported the full description of the preparation of amyl benzene in 1874 (Friedel and Craft, 1874).

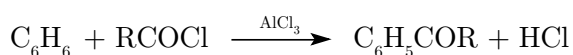
Friedel and Crafts' first findings were presented by Würtz to the Académie des Sciences on the session that took place on June 11, 1877, under the title *Sur une Méthode Générale Nouvelle de Synthèse d'Hydrocarbures, d'Acétones*, etc. (A new General Method of Synthesizing Hydrocarbons, Acetones, etc.) (Friedel and Craft, 1877abc). A steady stream of papers dealing with the new method followed this initial announcement, and by 1888 about fifty papers had been published in French journals. The original 3-page long memoir would turn into an 83-page long paper published in 1884, summarizing the large number of new chemical synthesis (substitution reactions) that had been realized using the new reaction, and another 39-page long published in 1888 and devoted to addition reactions (Friedel and Crafts, 1884, 1888b).

The Friedel-Crafts reaction, in its original form, was used to prepare substituted aromatic hydrocarbons by condensing, under the action of aluminum chloride, a halogenated aliphatic derivative with an aromatic hydrocarbon (Friedel and Crafts, 1884):



Friedel and Crafts reacted methyl chloride with benzene and obtained not only toluene but also series of methylated benzenes, which included xylenes, mesitylene, durene (1,2,4,5-tetramethylbenzene), and higher derivatives. Émile Ador (1845-1920) and Albert Rilliet (Ador and Rilliet, 1879) studied the different isomers formed by these reactions and Friedel and Crafts determined their physical constants and chemical reactions. Benzyl chloride with benzene yielded diphenylmethane that Ernst Theodor Zincke's (1843-1928) (Zincke, 1873) had obtained by the reaction of zinc dust and benzyl chloride, chloroform and benzene yielded triphenylmethane, and carbon tetrachloride and benzene yielded tetraphenylmethane (Friedel et al., 1881; Friedel and Crafts, 1882).

Similarly, ketones were produced from an acid chloride (aliphatic or aromatic) by condensation with an aromatic hydrocarbon:

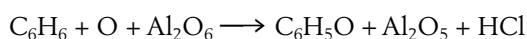


Benzene with acetyl chloride yielded acetophenone, and with phosgene (carbonyl chloride) benzophenone. Afterwards, Adolph Emmerling (1842-1906) and Carl Ostwald Viktor Engler (1842-1925) succeeding in synthesizing indigo from acetophenone, by nitration followed by dehydration

and reduction with soda lime and zinc dust (Emmerling and Engler, 1870).

The reaction was also tested successfully with other chlorinated compounds such as sulfur dichloride and phosphorus trichloride (Friedel, 1878) and used to demonstrate that in the presence the chlorides, bromides, and iodides, a variety of organic functional groups reacted with aromatic hydrocarbons to yield a large assortment of hydrocarbons, ketones, and organohalogen derivatives.

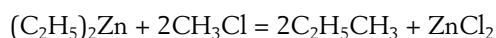
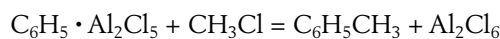
In a following publication Friedel and Craft described a different course of their reaction, where several simple bodies, radicals, or acid anhydrides became attached to benzene or its homologues (Friedel and Craft, 1888a). Here, in a crude picture, there was no elimination of hydrogen chloride: $\text{C}_6\text{H}_6 + \text{O} = \text{C}_6\text{H}_5\text{OH}$ but in practice hydrogen was released, except that this time the chlorine came from the aluminum chloride:



Treatment of the product of this reaction with water destroyed the intermediate complex with formation of phenol. Clearly, in this type of reaction aluminum chloride was not acting only by its presence (standard catalyst) but participated in the reaction without possibility of recovery and had to be used in the appropriate stoichiometric amount.

Thus, passing a current of oxygen through benzene or toluene in the presence of aluminum chloride yielded phenol or cresol; addition of sulfur to benzene in the presence of aluminum chloride yielded thiophenol and other phenyl sulfides, addition of carbon monoxide produced benzoic acid, sulfur dioxide yielded phenyl sulfonic acid, ethylene produced ethyl-, diethyl- and triethylbenzene, etc. etc.

Friedel and Crafts ended their memoir with a discussion about the possible mechanism of the reaction. Their experimental information indicated that aluminum chloride did not combine with hydrogen chloride, hence the possible explanation of their reaction was the formation of a small amount of an organometallic combination of aluminum, with elimination of hydrogen chloride, $\text{C}_6\text{H}_6 + \text{Al}_2\text{Cl}_6 = \text{C}_6\text{H}_5 \cdot \text{Al}_2\text{Cl}_5 + \text{HCl}$. Once this intermediate was created, it reacted with the organic chloride yielding two univalent radicals and regenerating the aluminum chloride, as the reaction between an alkyl chloride with diethyl zinc:



This mechanism was supported by the fact that the weight of hydrogen chloride released matched precisely the amount of chlorine contained in the alkyl chloride. Friedel and Crafts remarked that their reaction took place between an aromatic hydrocarbon and an alkyl chloride or an aromatic chloride carrying the chlorine atom in a side chain. It did not take place between, for example, chlorobenzene and benzene, chlorobenzene and an alkane, or an alkane and a chloro alkyl.

Friedel and Crafts tried without success to isolate the intermediate complex hence they went on to synthesize aluminum triphenyl; a compound they felt should have a similar action as the pretended complex. Aluminum triphenyl was synthesized by reacting aluminum with mercury diphenyl at 125°–130°C. Reaction of aluminum triphenyl with benzyl chloride gave diphenylmethane; with oxygen, phenol; and with sulfur, phenylmercaptan, but had no action on halogens substituted in the benzene ring. Hence a well-known organo-metallic compound gives the same reactions as aluminum chloride and benzene (Friedel and Crafts, 1888a).

Friedel and Crafts' explanation assumed that the formula of aluminum chloride was Al_2O_6 , but Lars Frederik Nilson (1840-1899) and Sven Otto Pettersson (1848-1941) (Nilson and Pettersson, 1887) had recently reported that according to Viktor Meyer's (1848-1897) method the molecular weight of the salt pointed to the formula $AlCl_3$, that is, aluminum was trivalent (the Meyer method is based on measuring the volume of occupied by a given mass when volatilized). Given the theoretical importance of the subject, Friedel and Crafts decided to perform their own measurement claiming that the Meyer method was unsuitable because it required operation at a temperature (440°C) well above that of the normal boiling point of the compound (183°C). Friedel and Crafts determined the vapor pressure of aluminum chloride at different temperatures, and measured very precisely its melting and fusion point. With this information they measured the density of the vapor using Jean-Baptiste André Dumas' (1800-1884) method, modified for different tensions, and found it to correspond with that required by the molecular formula Al_2Cl_6 . They speculated that at higher temperature aluminum chloride decomposed into two gases, which would explain the results of Nilson and Pettersson (Friedel and Crafts, 1888b). Today we know that aluminum is a tri-covalent compound in which the outer shell of the aluminum is incomplete. The combination of the aluminum chloride with the alkyl chloride complete the octet atom and given an addition compound in which the alkyl radical has a positive charge. The latter has a strong attraction for the electrons of the benzene ring and this provides the driving force for the reaction between the two compounds.

Friedel and Crafts promptly realized the industrial potential of their discoveries and proceeded to patent them (Friedel and Crafts, 1877de).

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