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Georg Wittig: The perfect symphonist in organic chemistry

Georg Wittig was a German organic chemist who discovered, in 1953, how a family of organic compounds, which are called ylides, could form the basis of the Wittig reaction, which easily causes two carbon atoms from different molecules to form a double bond. The Wittig reaction is a chemical reaction between an aldehyde or a ketone with a triphenylphosphonium ylide, referred to as the “Wittig reagent”, which produces an alkene and triphenylphosphine oxide side product. The key step of the mechanism of the ylide reaction is the nucleophilic addition of the ylide to the electrophilic carbonyl group, which forms a 4-membered ring that dissociates into the product molecules. The Wittig reaction is one of the most common techniques to prepare stereoselectively alkenes. The process has been used to synthesize important classes of substances such as biological pesticides, vitamin A, and related compounds for many foods and animal feeds, vitamin D derivatives, and steroids. Because of the Wittig reaction, such compounds can easily be synthesized on an industrial scale (BASF). Wittig is a primary contributor to the progress of organic syntheses in the 20th century because of the use of derivatives of nearly all elements in the periodic table, such as reactions with triphenylborane, phenyllithium, and triphenylphosphine. He also discovered the directed aldol condensation.

Wittig was a member of the French Academy of Sciences. On the occasion of the 350th anniversary of this institution, which has recorded many great achievements in the field of science, particularly chemistry, Wittig was honored. The scientific work of Wittig is nearly overwhelming. He was a universal scientist who had looked into the future of chemistry with the belief that new frontiers would introduce new opportunities for chemistry in science and industry.

1. Spectacular breakthrough and career

Wittig was born on 16 June 1897 in Berlin to an artistic family; his mother was a musician, and his father was a painter. He was born in the same year as the physicist

Cockroft (who received the Nobel Prize in Physics in 1951) and in the very year Thomson discovered the electron and its properties. Because his father worked in Kassel as a professor of applied arts at the high school, the entire family moved to this city. He attended high school (*Wilhelmsgymnasium*) in Kassel. Although it was a highly artistic and cultural atmosphere and his mother encouraged Wittig to play the piano, he decided to study chemistry. In 1916, he was enrolled to such studies at the University of Tübingen. His career was interrupted by World War I. Between 1916 and 1919, he was drafted and became a lieutenant in the cavalry of Hesse-Kassel and was subsequently made a prisoner of war by the British (1918–1919). One problem followed another, because after the war and his return to Germany in 1919, Wittig found admission by a German university difficult. Following several rejections, he finally was accepted by Karl von Auwers, a professor of organic chemistry who, at the time, was the director of the Chemical Institute in Marburg. *Ecce homo! Ecce homo!* Karl von Auwers! Wittig continued his studies in chemistry at the University of Marburg between 1919 and 1923 with him and was awarded a Ph.D. in organic chemistry in 1923. Encouraged by Auwers, he decided to continue an academic career. He became an assistant professor (*Privatdozent*) in 1923 at the University of Marburg. Between 1923 and 1926, he worked for his *Habilitation* at the University of Marburg. He remained an assistant professor there until 1932. There, he and Karl Ziegler (a 1963 Nobel laureate in chemistry) became life-long friends. Both were rock climbers in the Alps. He was also a friend of Walter Hückel, a professor of chemistry in Breslau and later Tübingen. In Marburg, Wittig married Waltraud Ernst, who also worked in von Auwers' group. They had three daughters. Waltraud Wittig, who also had a doctoral degree, took great interest in the scientific work of her husband, Georg Wittig. Wittig received his first permanent position as “Außerplanmäßiger Professor” in 1932 at the Technische Hochschule in Braunschweig. However, this period of time there proved to be a difficult period in

Wittig's academic career. In Braunschweig, there was a strong Nazi presence among the professors at that time. Karl Fries, who was well known for the discovery of Fries rearrangement and the director of the institute, opposed the Nazi regime and was forced to retire. Wittig supported Fries and feared that he would also lose his academic position, but he remained in Braunschweig until 1937. In 1937, he followed the invitation of Hermann Staudinger (who received the Nobel Prize in Chemistry in 1953), who was the director of the Chemical Institute at the University of Freiburg im Breisgau, to become an associate professor. Staudinger also refused the Nazi regime and had to suffer under political pressure, but he could hold his position in this difficult period because of his high scientific reputation. Notably, Wittig supported Staudinger's concept of high polymers in his *Stereochemie*. Wittig remained as an associate professor in Freiburg between 1937 and 1944. In 1943, Wilhelm Schlenk died, and the faculty of the University of Tübingen nominated Wittig as his successor there. He was appointed a full professor and director of the university's Chemical Institute. Finally, at the age of forty-seven, in 1944, he moved to the University of Tübingen as a professor and remained there until 1956. In 1956, Wittig moved once more to become a professor and the successor of Karl Freudenberg at the University of Heidelberg and the director of the Institute of Organic Chemistry at this university. Herein, he established a group with more than forty members and remained there until his formal retirement in 1967.

2. Cogito ergo sum

The most important discoveries of Wittig occurred between 1937 and 1956. Wittig is well known in the history of science for the Wittig reaction and the Wittig rearrangement. The mechanism of the Wittig reaction has long been a contentious issue in organic chemistry. The scientific research of Wittig was marked by the chemistry of his academic teacher, von Auwers. Wittig aimed to enter new fields in chemistry, and his objective was to find highly strained three- and four-membered ring systems with a tendency to form diradicals. At that time, the available physicochemical methods did not help to detect radicals, and this subject of research was notably difficult. Notably, Wittig's interest in radicals significantly affected his further scientific work because it led him to organometallic chemistry. In chemical synthesis, as starting materials, he used sterically hindered compounds with phenyl groups, which were synthesized by the classical reaction of Grignard compounds to ketones. The wise Wittig decided to use phenyllithium, which was proven to be superior to phenylmagnesium bromide. This decision was life changing! In this way, Wittig created a new field of "carbanion chemistry", which was later named "organometallic chemistry" or "carbanionoid chemistry". He observed the exchange of hydrogen for lithium and the exchange of bromine against lithium; the metalation and halogen–metal exchange reactions were published in 1942. He remarked that the treatment of fluorobenzene with phenyllithium gave interesting products, which led Wittig to propose dehydrobenzene C_6H_4 as a reactive intermediate in

1942. The Wittig rearrangement has an interesting mechanism and a broad scope of application, which is discussed in modern textbooks of organic chemistry. The success with phenyllithium led Wittig to start another research project in Freiburg. He sought to overthrow the octet rule for nitrogen compounds, and he attempted to prepare the pentavalent compounds, tetramethylphenyl nitrogen, and pentamethyl nitrogen. As a result of his efforts, he discovered a new class of ammonium ylides, and other researcher showed that the derivatives containing a lithium salt should be considered lithiated ammonium salts instead of ylides. Ammonium ylides undergo various rearrangements and elimination reactions. In the course of this work, Wittig always used benzophenone to determine the position of lithiation. This principle of obtaining crystalline derivatives to characterize sounds trivial, but this procedure using benzophenone led him to the discovery of the Wittig reaction in 1953. Wittig continued the work on hypervalent compounds of the elements in the 5–7 groups of the periodic table and synthesized pentaphenyl phosphorene and higher homologues tetraphenyltellurium and triphenyliodine. Triphenylphosphine oxide and 1,1-diphenylethylene were formed in high yield via the intermediate. A pioneering paper of Wittig with Schöllkopf was published, called "Über Triphenyl-phosphinmethylen als olefinbildende Reagenzien (I. Mitteil)" (1954; Triphenylphosphine methylene derivatives as reagents for the formation of olefins) in *Chemische Berichte*. Wittig's work was guided by the general idea of establishing the field of carbanion chemistry as equal in importance to the fields of free radical and carbonium ion chemistry. His studies led him to various new structures. Best known is his work on phosphorus ylides, which condense with carbonyl compounds to form alkenes.

After his formal retirement, Wittig worked on aromatic compounds and diradicals, in which he had been interested more than fifty years earlier as a young lecturer. These late studies of Wittig as a professor emeritus opened an elegant path for other authors, after his death, to dendrimers. A dendrimer is a member of a modern class of macrocycles.

During his long career, Wittig also had great success as a mentor, and he encouraged many young scientists to start an academic career. More than three hundred graduate students and postdoctoral colleagues were associated with work with Wittig. He recognized a universal scientific demand for a renewed alliance between science and students/colleagues and the sharing and transfer of its knowledge to colleagues.

Between 1953 and 1979, Wittig received many awards, honorary doctorates, and other forms of recognition. The Adolf von Baeyer Memorial Medal was awarded to him by the German Chemical Society in 1953. He was the first German after World War II to receive an honorary doctorate from the Sorbonne, in Paris, in 1957. He received Honorary Doctorates from the Universities of Tübingen and Hamburg in 1962, the Silver Medal from the University of Helsinki in 1957, the Dannie Heinemann Award from the Göttingen Academy of Sciences in 1965, the Otto Hahn Award for Chemistry and Physics in 1967, the Silver Medal from the City of Paris in 1969, the Paul Karrer Medal from the University of Zurich in 1972, the "Médaille de la chaire

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