GEORGES DARZENS (1867–1954): INVENTOR and ICONOCLAST

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Georges Darzen's name is absent from the *Dictionary of Scientific Biography*. This is a regrettable omission, on three grounds. He was a creative organic chemist, to whom we owe both the thionyl chloride conversion of alcohols into chlorides and the "Darzens reaction"—an addition-fragmentation which can be seen as the forerunner to the Wittig reaction. He was a perceptive observer of the scientific scene, keen on informing his students of the latest scientific developments during the first quarter of this century regarding the structure of the atom and the quantum theory of spectra. And this genuine Renaissance man, by his multi-faceted talents, by the diverse degrees he took, by his prolific academic and industrial activities, was also endowed with a remarkable independence of spirit. Thus, we offer here a summary of his life and work.

Early Years

Georges Auguste Darzens was born on 12 July 1867 in Moscow. His family came from the Aude region in Southern France. His father, Amable Rodolphe Darzens (1823–1886), settled in Moscow, following there cousins who probably came from France when Napoleon invaded Russia. The father was engaged in trade between the two countries.

Sent to Paris for his education at the age of 13, Georges Darzens became a boarder at Collège Sainte-Barbe. He prepared there for the competitive examination to the École polytechnique, where he studied (class of 1886) before becoming a professor (1913–1937). During his studies at the École, he was attracted to astronomy. However, this budding vocation was quashed when the medical staff diagnosed eyesight problems and gave Darzens glasses to correct them. At that time, unless a student completed the École polytechnique curriculum with a very high ranking (the first 15 or 20 would enter government service as high-level technical councilors), he would be inducted into the French Army. Most Polytechniciens became Army captains and served out life-long careers within the military. Not so with Darzens—even though his final rank was 39th out of a class of 226, his poor eyesight spared him from an Army commission.

Turned away from astronomy, Darzens embraced chemistry. His mentor at the École polytechnique, Édouard Grimaux (1835–1900), was at the time of Darzens's studies (1886–1888) one of the few French organic chemists to disobey the decree of Marcelin Berthelot against teaching atomic theory. As Darzens would later write, "These atomistic theories, renovated by [Adolphe] Wurtz and his school, were responsible for my entering organic chemistry" (1). During the period 1888–1897, Darzens served as an assistant to Grimaux in his laboratory at École polytechnique.

At that time, another former Polytechnicien became world-famous. Captain Alfred Dreyfus had been convicted of treason to his country and had been sentenced to Devil's Island in French Guyana. Grimaux and Darzens were both convinced of Dreyfus's innocence and they vigorously supported his cause. This took considerable courage in the military milieu at École—they were voices crying in the wilderness—and they suffered for their stand. Grimaux was even summarily dismissed from his chair.

The Renaissance Man

Conventional wisdom sees old age as a slow-motion disaster. Young adulthood, however, is seldom a success

Georges Darzens, in the uniform of a student at École polytechnique, in 1887

story. The person has yet to firmly grab a career; and elders offer resistance. The Darzens biography magnifies the former stereotype. This young man was splendidly unfocused. His unbridled energy was daunting. He was helping Grimaux as an assistant and he later became *répétiteur* at the École. During the last decade of the 19th century, Darzens continued to explore various careers. Already in possession of a B.S. degree in mathematics, and of another in physics, he studied for, and in 1895 also passed, the *agrégation* in physics. This certification exam would have allowed him, had he so chosen, to teach in secondary schools. As if he were not busy enough studying chemistry, mathematics, and physics, all at an advanced level, in 1890 Darzens also enrolled in medical school, receiving his M.D. in 1899. He doubled up, in much more than a consulting position, from 1897 on, as director of the research laboratory of the L. T. Piver perfumery company—a position that he held until 1920. Yet another avocation of Darzens was physiological optics. As he later wrote (in the third person), "at the onset of his career, at a time when he was still undirected, he published (in 1895) a physical theory of the perception of colors by the eye" (2).

The Inventor

This was also the time of the birth of the automobile and Darzens launched himself into the new era with characteristic passion. While his brother, Rodolphe, was organizing the first car races (in which he also drove), Georges conceived, designed, and built three or four automobile prototypes in the period 1890–1910 (3). If Darzens was an inventor in his spare time, his inventiveness also marked him as a scientist. Following Vlado Prelog, one can classify scientists into four sub-groups: improvers of the state of knowledge; providers of general explanations for sets of facts; authors of discoveries; and inventors. Darzens clearly belongs with the last.

His chemical inventions include a general method for -OH to -Cl substitution, which Darzens himself described thus (2):

> . . . in order to prepare the α-chloropropionic ester, he has devised a novel procedure for substituting chlorine for the hydroxy group in a molecule. This procedure uses the action of thionyl chloride [$SOCl_2$] in the presence of a tertiary (amine) base. It has been put to universal use for performing such a substitution in fragile molecules such as terpene alcohols and sterols.

His inventive talent is also obvious from his contributions to the composition of perfumes and from his involvement in the development of explosives during the First World War (4). Appointed to Service des Poudres on 31 October 1914, Darzens immediately improvised a makeshift manufacturing process for making picric acid from aniline. This production was started at the end of 1914. By the time of the Battle of the Marne, he was submitting numerous classified reports to the scientific commission for powders and explosives.

Darzens's main contribution to chemistry is the reaction that bears his name. It puts him in the first rank of French organic chemists during the first half of our century, along with such names as Victor Grignard (5). I can do no better than to let Darzens himself (without undue modesty) summarize his contribution (6):

> As early as 1904, he set up the handsome method of glycidic synthesis of these two important classes of compounds, aldehydes and ketones. This method has become a classic and is in universal use. It bears his name.

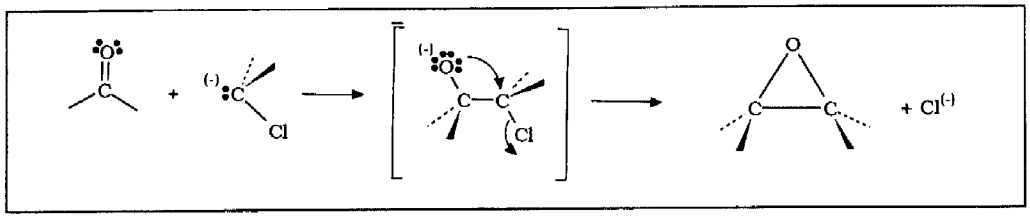

Figure 1 The Darzens reaction

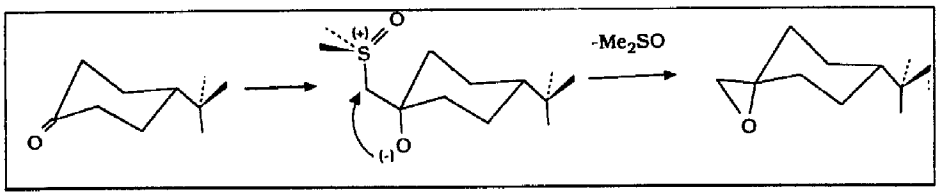

Figure 2 The Corey-Chakovsky reaction

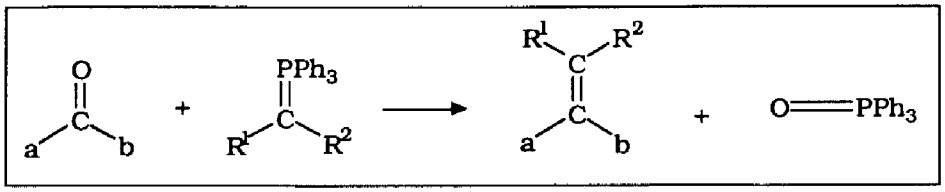

Figure 3 The Wittig reaction

This method consists in the condensation of α-chloro esters with ketones or with aldehydes under the action of sodium ethoxide or of sodium amide. In this manner one obtains glycidic esters that can be saponified easily into the corresponding acids. These are decomposed by a simple distillation into, depending upon the case, new homologous aldehydes or ketones . . . This glycidic method of synthesis, besides its exceptional generality, has led to preparation of the most diverse aldehydes and ketones in all fields of organic chemistry.

A continuous thread connects this reaction with other, more recent, name reactions. The Darzens reaction is an addition-fragmentation (Fig. 1). Among its other merits, it gives ready access to those activated and extremely useful intermediates—the epoxides. The first step is addition to a carbonyl of a chlorine-bearing carbanion. The second step is internal displacement of chloride ion by the back-side attack of the charged oxygen nucleophile produced in the first step. An epoxide results. The Corey-Chaykovsky modification (Fig. 2) uses a carbanion $^{(-)}CR_1R_2X$ in which the X leaving group is a stable, neutral entity—either dimethyl sulfide or dimethyl sulfoxide. Epoxides are also produced, and in a highly steroselective manner. The Wittig reaction (Fig. 3) adds a phosphorus ylid to a carbonyl. While it resembles in mechanism the Corey-Chaykovsky procedure, the Wittig reaction differs from it, because of both kinetic and thermodynamic factors, in producing an olefin (together with a phosphine oxide as the side-product).

The Educator

Darzens was a keen follower of new developments, not only in chemistry but in science in general. To give an outstanding example of his percipience, while the Millikan determination of electronic charge was performed during the period 1909–1913, Darzens included it in his very first lectures at École polytechnique in 1913–1914. Likewise, in the 1930s, his course in general chemistry juxtaposed the Mendeleev periodic classification and the shell model of the atom borrowed from J. J. Thomson and N. Bohr.

This taste of Darzens for the new and daring in science was very helpful to his institution. Quantum mechanics entered the École very late, with the appointment of Louis Leprince-Ringuet to a chair in physics in 1936. Fortunately, during the whole period between the two World Wars, when the physics professor, Lafay,

was deaf to new ideas and silent on relativity and quantum theories, Darzens's general chemistry teaching went some way toward filling the void. He made his students aware of the new discoveries in atomic physics. From the very first pages of his lecture notes, the reader learned about electrons, X-rays, and Rutherford's nuclear model of the atom.

Was the organic chemistry course also ahead of its time? If framed in the classic mode, it does not compare badly with that given by J. B. Conant at Harvard. Darzens brings in not only natural products with pharmacological activity and applications to industrial chemistry, but also cites compounds of potential military use. One of his comments reads: "very toxic and easily flammable, some spontaneously—phosphines might find use as aggressive compounds in warfare."

Another merit of his lectures is their historical dimension. Thus Darzens pays homage—and this was rare at the time—to the pioneering work of the Russian genius Mikhail Vasilievisch Lomonosov (7):

> Systematic observation of the numerical relationships between the various chemical phenomena seems to have had as its precursor the Russian chemist and writer Michael Lomonosov (1711–1765). Not only does this scholar introduce the concepts of relationships, but also those of volumes, of pressures, and of temperatures. He applied mathematical methods to the study of chemistry. He even developed, using the example of nitre, a theory of crystal structure that makes him the first crystallographer.

Darzens provided his students with a very modern presentation, not only relative to their outdated physics course, but also in an absolute sense. He was, for instance, very much interested in what we call "reaction mechanisms"—which he termed the "theory of a reaction."

The Nonconformist

Darzens had considerable self-assurance. While still a *répétiteur* at École polytechnique, he published a booklet on chemistry for the layman (8). The subtitle, "A Textbook Estranged from Any Program," was characteristic of him. As we already noted from his behavior during the Dreyfus affair, Darzens was brave and did not hesitate to take other unpopular and lonely stands. At a time when France was bent on revenge on Germany for its rout during the Franco-Prussian War of 1870, and at a time when it was deemed antipatriotic, if not treasonous, to praise anything German, Darzens expressed his admiration for German chemistry. With Cassandra-like lucidity, he was preoccupied by the economic and scientific advances of Germany as compared to those of France. He saw clearly that the vigorous health of the German chemical industry was rooted in a firm experimental basis (the laboratory training introduced by Liebig), in patent regulations that allowed protection of a new process (and not just the discovery of a new molecule, as in France), and in its methodical organization. There was at least one clash between the administration of the École and Darzens's publicly-expressed admiration for German chemistry during his first year of teaching; and the *directeur des études* had to tell him to be more circumspect (9). Apparently his unorthodox personal life and his militant Free-Masonry (he became a dignitary in one of the French branches), together with his other traits of independence, ensured that he was never elected to the French Academy of Sciences, to which he so obviously should have belonged.

Darzens retired from École polytechnique in 1939. In 1945, while he was attending a conference in Italy, his laboratory was taken away from him. His protest letter to the German general then heading the École is a valu-

Georges Darzens, after his retirement, in the Luxembourg Gardens, in Paris ca. 1940 (picture by Brassai)

able document for the historian, as Darzens uses it to summarize the highlights of his teaching carrer at the École. Despite this loss, he continued to address himself to chemical problems, publishing communications in *Comptes rendus de l'academie des sciences* until the early 1950s. During his last years, he continued to enjoy Parisian life, going to the Opéra and Opéra Comique, continuing to work on some of his pet projects outside chemistry (major scientific problems, such as the expansion of the Universe, a theory for lepra, and one for cancer), having a very active social life (he loved the company of people and especially that of women), and running a complex personal life. He died on 10 September 1954.

His Vision of Chemistry

Early in his career, Darzens—who wrote a handsome prose—proposed this metaphor (8):

> The chemist appears to me in the guise of a traveller climbing on an endless mountain. Clouds mask the perspective. Glimpsed from afar, those trees, he fancies, are his goal; and those grandiose landscapes beyond which nothing is apparent. However, as soon as he gets there, as soon as he has traversed the fog, other horizons spring up beyond this first horizon. They are wrapped also in the same deceiving haze. And our chemist is infected with the crazy desire to progress yet further. He covets getting to a point where he alone will be left to admire the splendors now left behind him. Indeed his temerarious and haughty climb gives him so many wonders to look at that they enthrall him. He catches himself fantasizing about what may lie beyond and his intuition does not betray him.

This accurate report of the joy of discovery from an extremely creative scientist is worthy of the attention of psychologists.

Darzens made other extremely interesting statements about chemistry. He saw it as a science lying somewhere between the empirical and the mathematical (10):

> Convinced that chemistry had much to gain from acquiring general methods to solve its numerous problems, that differ much more by their appearance than in their intimate nature, I developed the desire to devote myself to such a study. The reader will find out that most of my work aimed at establishing such general methods. *They are to chemists the equivalent of equations to mathematicians.* I have met with a degree of success.

This reflected his deep ambivalence towards organic chemistry. Sometimes he compared it to mathematics for its inner logic and for lending itself to formalization, whereas, at other times, he put the accent on the unavoidable empiricism (11):

> Its domain remains much more that of intuition than of rigorous deduction. Its practitioners need to become steeped in a peculiar form of knowledge. It is more akin to a "wisdom" than to a "science"; and it is acquired only through lengthy and almost physical intimacy with chemical substances. HERE ONE THINKS WITH ONE'S HANDS ought to be engraved on the entrance to all our laboratories.

Besides such insights into the nature of organic chemistry, Darzens had other incisive remarks, as when he noted that (10):

> The greatest advances have occurred whenever a new inorganic reagent has been introduced in organic chemistry.

ACKNOWLEDGMENTS

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NOTES AND REFERENCES

1. G. Darzens, *Recherches et trauaux scientifiques de M. Georges Darzens*, J. Dumoulins, Paris, 1912, (printed résumé presented by Darzens as a candidate to a chair in chemistry at École polytechnique).
2. "Note sur les travaux scientifiques de M. G. Darzens, "undated manuscript, c 1949, possibly prepared in support of yet another, aborted candidacy to the French Academy of Sciences, to which Darzens was never elected; kindly communicated to the author by Dr. Jean Jacques.
3. One of these designs led to a small series of six to ten vehicles. The innovations Darzens introduced were the lengthening of the ride of the pistons with respect to the "square" arrangement that had been the norm till then; the introduction of ball bearings in the hub of the wheel, that met with his friend Louis Renault's utter skepticism: "You are making a mistake! Roller bearings are no good, nothing beats a smooth hub;" and the equality of the sizes of the front and rear wheels.
4. While at Piver, he designed such classic perfumes as "Floramye" and "Tréfle Incarnat." Later on, having moved to other companies, he continued formulating

successful perfumes at Grenoville (1921–1924) and at Dior (1926–1931). During the latter period, he started the manufacture of various synthetic nitro musks.
5. P. Laszlo, "Un grand Polytechnicien, Darzens (1867–1954)", *La Jaune et la Rouge*, **1988**, 18–20.
6. Reference 2.
7. G. Darzens, *Cours de chimie générale*, École polytechnique, Paris, 1913–1914, p. 3.
8. G. Darzens, *Initiation chimique*, Hachette, Paris, 1912.
9. P. Laszlo, "Le Chatelier, Public Prosecutor of Darzens," *Ambix*, in press.
10. G. Darzens, *Cours de chimie générale*, École polytechnique, Paris, 1919–1920 (emphasis added) .
11. G. Darzens, *Cours de chimie organique*, École polytechnique, Paris, 1937–1938, p. 11.

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