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A Profitable Partnership

Giacomo Ciamician and Paul Silber

The development of modern science has had many important and fruitful cooperating contributors—Liebig and Wöhler, the Curies, and Gay-Lussac and Thenard, to name but a few. None of these partnerships achieved a level of productivity and accomplishment approaching that of Giacomo Ciamician (1857–1922) and Paul Silber (1851–1932). In more than 35 years of cooperation and friendship, the Armenian Ciamician and the German Silber raised the stature of chemical research in their adopted Italy to world renown. In a succession of at least 378 scientific publications they discovered a valuable antiseptic; developed a pyrrole-pyridine ring expansion; added contributions to terpene, essential oil, and pyrrole chemistry; and virtually initiated the field of organic photochemistry.

The Beginnings of the Partnership

This profitable partnership had its origin in the 1880's in the laboratories of Cannizzaro at the Institute of General Chemistry in Rome. Here the young Ciamician, fresh from his studies with Barth and Weidel in Vienna and from his doctorate in Giessen, met Paul Silber, newly arrived in Italy for reasons of health.

Silber, who was born in Stargard, Pomerania, in 1851, had just received his PhD from the University of Freiburg for a thesis on the synthesis of diethyl glycolic acid and its derivatives. He had spent a short time as an assistant to Erlenmeyer and two years as a dye chemist at the Marienberg Dyeworks. In 1881 both he and Ciamician came to Italy to join the enthusiastic group of researchers gathered about the master, Cannizzaro.

Ciamician had already displayed a mastery of both theoretical and experimental chemistry. While pursuing his studies in Vienna, he had published a series of brilliant papers on emission spectroscopy, vapor density determination, animal resins, and air pressure in tubes.

His pioneer work in spectroscopy demonstrated that elements of the same periodic family possessed strikingly similar emission spectra. Lacking an understanding of the yet undescribed electronic energy levels in the atom, he developed a rational, and not entirely incorrect, theory that each member of the family possessed some common components which were responsible for the spectral similarities.

The explanations of emission spectra, proposed by an unknown young chemist just turned 20 and not yet in possession of his PhD, were discussed before meetings of the Viennese Academy and even translated by Professor Ira Remsen for the initial volume of his *American Chemical Journal*(1).

At the University of Vienna, and later at the Chemical Institute in Rome, Ciamician developed his ideas on spectroscopy into what was probably the first formal course on the subject.

After transferring to Giessen, because it was the only university which accepted students without a required prior diploma in classics, he received his doctorate in 1880 and joined the Cannizzaro group in Rome. For the next seven years he concentrated almost entirely on pyrrole chemistry and in 1887 was awarded the Royal Academy of Lincei prize for his discoveries.

In 1887 he was offered a post at the University of Padua, and two years later the University of Bologna called him to a professorship. Silber accompanied him to these universities and was later appointed as an Honorary Colleague of the Faculty of Science at Bologna.

For the next 25 years, until World War I ended their partnership, their united research efforts bore the characteristic marks of each member's contributions. Ciamician, as the genial and critical research director, applied his theoretical and practical insights to organizing the direction of the program and interpreting its results. Silber, as the skilled and patient experimenter, provided the abundant results upon which they founded their joint careers.

Autographed portrait which Ciamician presented to students who submitted perfect examination papers.

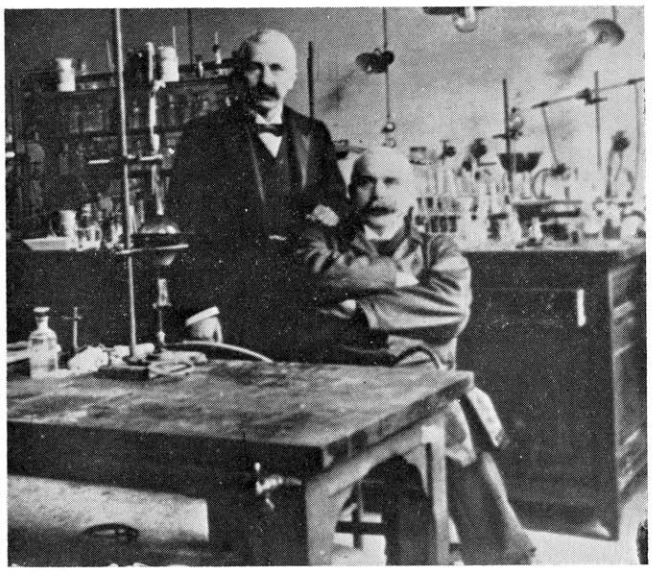
In 1885 Ciamician and Silber announced the preparation of a new potent antiseptic with valuable therapeutic properties: tetraiodopyrrole. After patenting their discovery(*2*), Ciamician wrote a series of articles on the preparation, properties, and photodecomposition of the substance which he named "Iodol." Many years later Iodol was still in wide use as an iodoform substitute, and Valentin stated that unquestionably its discovery was one of the most important contributions to the science of pharmacology(*3*).

Natural Products

When Ciamician and Silber left Rome for Padua and Bologna, most of their contributions to pyrrole chemistry had been concluded. Ciamician summarized their work in this area with a classic publication entitled "The Development of the Chemistry of Pyrrole in the Last Quarter of a Century," which he delivered before the Deutsche Chemische Gesellschaft(*4*).

In Padua and Bologna, Silber's efforts were directed toward Ciamician's latest interests, the organic components of vegetable matters and photochemical reactions.

In the area of terpenes and essential oils, they published more than 70 articles on the isolation and characterization of apiole, safrole, eugenol, isosafrole, isoeugenol, pseudopelletierine, and many other naturally occurring phenolic compounds. Many of these natural substances were subjected to detailed chemical investigations and their rearrangements and isomerizations described. The partners reported the base catalyzed transformation of eugenol to isoeugenol, a process which became of utmost importance in the synthesis of vanillin.



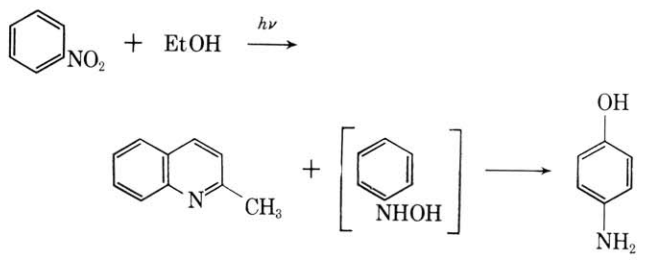
Giacomo Ciamician (standing) and Paul Silber in their Bologna laboratory

Ciamician, meanwhile, found time to pursue his own interest in theoretical and physical chemistry. He published his views on the true structures of benzene, naphthalene, pyrrole, and other five-membered rings. He attempted to correlate similarities of compounds known to form solid solutions and to relate the physical properties and structures of benzene and thiophene systems.

Organic Photochemistry

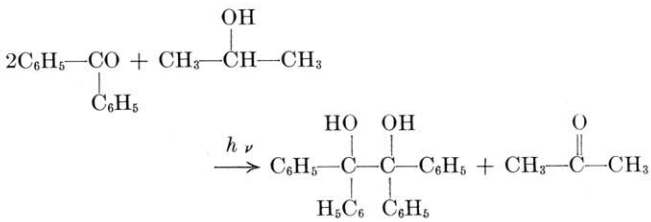
At the close of the century, Ciamician decided to abandon his previous researches in natural products and to embark on a systematic study of the chemical action of light. His reasons for venturing into the almost virgin area of organic photochemistry have never been stated, but it appears that he was influenced by at least two factors.

First, photochemical effects were not really new to him. While he and Silber were serving as assistants in the Cannizzaro group, they had published two remarkable light-catalyzed reactions. Almost simultaneously with Klinger, Ciamician observed the photoreduction of benzoquinone to hydroquinone by alcohols. With his exceptional experimental skills, Silber was able to demonstrate that irradiation of nitrobenzene in ethanol produced a complex mixture of nitro reduction products in which *p*-aminophenol and quinaldine were major



components. Ciamician called this a "photochemical Skraup synthesis" and rationalized that the quinaldine resulted from condensation between the ultimate photoreduction product, aniline, and the photooxidation product, acetaldehyde (or crotonaldehyde).

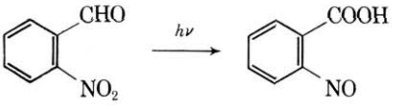
Second, Ciamician encountered an article by two French workers on the irradiation of benzophenone in alcoholic medium. Because of an inaccurate combustion analysis and a lack of chemical degradation studies, they described their material as a condensation product of benzophenone with acetaldehyde(*5*). Recalling his own previous work on photoreduction–oxidation reactions, Ciamician hastened to repeat this study and to establish firmly the structure of the benzophenone irradiation product as benzopinacol. Although Ciamician and Silber did not in fact discover this useful and widely applied photosynthesis, they are generally given the credit because they were able to recognize the structure of the photodimer.



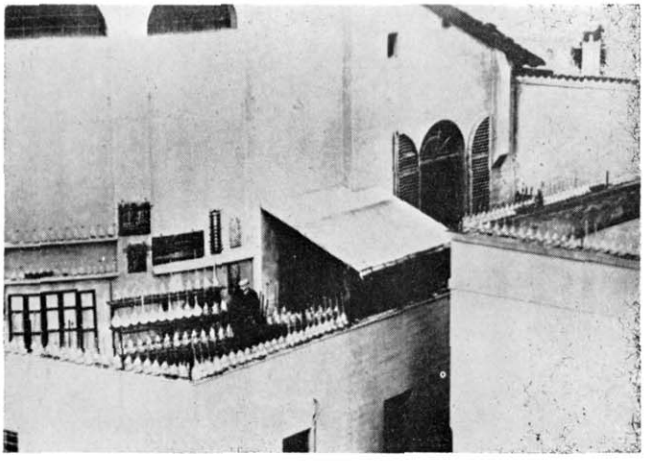
For the next 15 years the Ciamician-Silber duo published 85 notes, papers, and memoirs on what was probably the first systematic study of the behavior of organic compounds toward light. In the course of their extensive investigations, entitled in the German literature "Chemische Lichtwirkungen," they discovered many new and unique light-catalyzed reactions still being

studied today. They explored photoreductions of aldehydes, ketones, quinones, and nitro compounds in alcoholic media, photoisomerizations about double bonds, olefin dimerizations, and photo-hydrolytic fragmentations of ketones.

An example of an intramolecular oxidation-reduction phenomenon was discovered in the irradiation of *o*-nitrobenzaldehyde. In an extraordinarily rapid photo reaction—Ciamician compared it to a photographic process in its speed—the nitro function was reduced to a nitroso and the aldehyde oxidized to a carboxylic acid. Mechanistic studies on the reaction have entertained chemists ever since(*6*).



During a study of the dimerization of olefins—to which Ciamician applied the general term "polymerization"—a unique type of internal cycloaddition was discovered(*7*). The monoterpene carvone, which possesses two double bonds in relatively close proximity, was shown to undergo transformation to carvone camphor. Although Ciamician could not conclusively establish its structure, his knowledge of the course of similar reactions led him to favor strongly the structure which Buchi eventually demonstrated to be correct(*8*).



Ciamician surveys his collection of tubes and flasks being exposed to the sun on the roof of his laboratory.

Popular Pamphlets and Booklets

Lecturing before the Société Chimique de France on June 6, 1908, Ciamician reviewed the subject of organic photochemistry and summarized his own work in the field. During these years of study on light-catalyzed reactions he left more and more of the laboratory problems to Silber and began to record his ideas and theories in a series of short booklets, reprints of lectures he presented before learned societies of Europe and America.

"Chemical Problems of the New Century," "Problems and Objectives of Today's Organic Chemistry," "Cooperation of the Sciences," and "Organic Chemistry in Organisms" were published between 1903 and 1911 and found wide acceptance among students, laymen, and practicing chemists.

Ciamician's prophetic lecture in 1912 on "The Photochemistry of the Future"(*9*), presented before the International Congress of Applied Chemistry meeting in New York, was hailed as a classic many years after its delivery. With the exception of tides, which he believed could never be efficiently harnessed, and atomic energy, which he foresaw as a force that "will surpass by far the limits assigned today," he judged all known sources to be inferior to natural sunlight. He predicted solar home heating, photo-electric batteries, increased agricultural utilization of light, and industrial and synthetic applications of solar fuel. In addition, he reviewed his own photochemical contributions and those of "my friend Dr. Paul Silber"(*10*).

The long partnership in Bologna was ending. With the 1915 Declaration of War between Italy and Germany, Paul Silber, then 64 years old and a resident of Italy for almost 35 years, decided it would be safer to remove his family from Italy for the duration of the war. Ciamician was unable to bring himself to a parting at the station. He summoned his two assistants, Ciusa and Ravenna, who had been drafted into the Italian army, asked them to remove their uniforms and escort the Silber family to the train as evidence that they were friends first and Italians second.

At the end of the war Silber returned to Bologna where he assumed a position as scientific director of Istituto Neoterapico Italiano.

Ciamician, exhausted from his labors for his beloved Italy during the war, succumbed to a fever in the fall of 1921. Against the advice of students and friends he attempted to begin his organic and general chemistry lectures, but the illness soon conquered. He died on January 2, 1922. Silber survived until 1932, when he passed away in Bologna at the age of 81.

The contributions of Ciamician and Silber to modern chemistry should not be measured by mere numbers of publications. The new areas which they opened and explored have attracted numerous investigators in pyrrole and natural products chemistry and in theoretical and photochemistry.

Acknowledgments

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