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GIUSEPPE BRUNI

1873–1946

BY MARIO A. ROLLIER

Twenty-five years ago, in 1923, the chemists of Yale, Columbia and Ohio Universities, as well as of the Mellon Institute, had the opportunity to hear through the living voice of Giuseppe Bruni a series of lectures[1] which he delivered on "Solid Solutions."

Starting from van't Hoff's theories, Bruni in his lectures gave an extremely cogent exposition of all that was known on the solubility in the solid state at that time and which had been in large part due to his own contributions. He treated the subject from the several points of view of the diffusion in the solid state, the heat of formation of solid solutions, their constitution and the applicability of the laws of solutions to solid solutions. In these lectures and the resulting monograph Bruni condensed the results of twenty-five years of study, research and widespread scientific coöperation on the subject.

Having thus pointed out what is Bruni's chief claim to be remembered in the chemical world, it is timely to add something on his very brilliant scientific and academic career. Bruni was born on August 25, 1873, in Parma (Northern Italy). Immediately after he received his doctor's degree at Parma in 1896, he entered the best Italian School of Chemistry of that period, the Institute of Ciamician at Bologna University, the general trend of his research being already chosen (isomorphism and solid solutions) in his first paper. He remained with Ciamician for ten busy and quiet years, only interrupted by his trip to Germany and the long visit he paid to van't Hoff at Wilmersdorf in 1900–1901. During this decade he had the opportunity of applying the phase rule to the field of concentrated solid solutions, reaching the same results which Bakhuis-Roozeboom had arrived at independently, and gave proof of his clear and synthetic mind in a monograph on the general subject of his research, published in Germany in 1908 under the title "*Feste Lösungen und Isomorphismus.*" A few years before van't Hoff had occasion to pay a tribute to Bruni's contribution in this field, stating:

Ce savant a contribué d'une partie prépondérante à l'adoption des lois sur les solutions solides et les mélanges isomorphes, qui, sans son intervention auraient été troublées par des notions confuses.

Many years before Bragg and Laue's discoveries opened the road to modern structural chemistry, Bruni had already said that the distinctive function of the chemist, as compared with the physicist and the mineralogist, was to discover and explain chemical constitution and to use all the available data in the fields of isomorphism, crystallography, energetics, etc., to solve chemistry's central problem, namely, from physical properties of a substance to deduce and to predict the constitution and the actual position of atoms inside its molecules. What already had been van't Hoff's was also Bruni's chief concern: the position of

(1) Published with the same title in *Chem. Rev.*, I, No. 4, January, 1925, page 345.

atoms in space (*Die Lagerung der Atome im Raume*).

In 1907 Bruni was called to the University of Padua as full Professor of General and Inorganic Chemistry, and there he taught and worked for another active decade, advocating in the dispute between the "atomists" and the "energetists," the real existence of atoms and issuing accurate and valuable papers on diffusion in the solid state both in alloys and in ionic salts, and on the limits of validity of the cryoscopic method. The same year he became one of the founders of the periodical of scientific synthesis called "SCIENTIA" in which he was able to secure the active collaboration of such scientists as Russell, van't Hoff, Arrhenius, Nernst, Langevin, Poincaré, Ciamician and many others.

During World War I Bruni entered the arena of industrial chemistry, being first appointed chief consulting chemist and then chief of the Research Laboratories of "Pirelli," the rubber and tires manufacturing company. This appointment was connected with his discovery of ultra-accelerators for rubber vulcanization. Bruni's process of rapid, cold vulcanizing (1919) is based on the formation inside the rubber of N,N-diphenylthiourea (thiocarbanilide) bringing carbon disulfide to act on aniline in the presence of sulfur and zinc oxide. A few months later W. Bedford and W. Scott were obtaining the same results in the Goodyear Laboratories starting from piperidine instead of from aniline.

After the end of the war Bruni traveled extensively on behalf of the Pirelli Company, visiting Java and Malacca in 1921 and, in 1923 staying for a rather long time in the United States where he made connections which he held very dear and which he liked to recall, such as his acquaintance with Dr. Charles L. Parsons, the former Secretary of the American Chemical Society.

To the same period belongs one of the most important achievements of Bruni's scientific leadership: prepared as he was by his past works, he saw the decisive importance of X-ray investigations for the knowledge of the solid state. He sent Professor G. R. Levi, then his assistant, to Professor Debye in Zurich, and shortly thereafter the first laboratory equipped with all the necessary tools for X-ray structural research was operating in Italy at the Polytechnic School of Milan, whither in the meantime Bruni had been called as Professor of General and Inorganic Chemistry. For a little over twenty-five years Bruni was to teach chemistry at this Polytechnic School of Milan, an organization which, though on a smaller scale, comes nearest to something like the Massachusetts Institute of Technology.

Bruni is thus to be regarded as the founder of the Italian school of structural chemistry, to which scientists like G. R. Levi, G. Natta and A. Ferrari, all of them Bruni's students, belong, and which has done good and valuable work and has kept pace, under Bruni's influence and advice, with the developments of the newer techniques of structural research (electron diffraction, infrared spectra, dipole measurements, etc.).

Bruni was extremely brilliant in controversies involving industrial patents. His acute judgment was blended with humor and his advisory help was in great demand both in Italy and abroad. From his experience in this field, in his later years he turned his attention to the problems of intellectual property and in 1935–41 he published a series of papers on patent law, urging international recognition of the principle that "the inventor should have the right to patent an invention *even* if preliminary publications *by him* on the same subject were already circulating in the technical literature" and struggling for the introduction of the "provisional specification" in the Italian patent law.

Two months before Bruni died (January 3, 1946) he sent to the editors of "SCIENTIA" his last contribution, a letter on the large-scale use of nuclear energy in the atomic bomb, in which he hailed the event as the true beginning of a new era upsetting the balance of natural power at the disposal of mankind and scoffed with his customary clear-sightedness at the claims of "secrecy," all the secrecy being a question of industrial development and the theoretical basis of the large-scale transformation of nuclear in lower forms of energy being known. Though still without any connections with scientists of the western world, because of the war, he joined them in their deep concern about nuclear energy, writing:

> By far the most important problem is not that of the industrial applications of atomic energy but another one, which may be looked at with great anxiety. Will not the release of these formidable forces have a general and permanent influence on the world's economic arrangement, on its overall balance, both material and energetic, and on its evolution?

A question certainly yet unanswered.

Bruni earned many recognitions of his high scientific merit. He was awared the King's Prize for Chemistry by the *Academia dei Lincei* in 1913 and was elected a member of the same Academy in 1917. He was a member of the American Chemical Society from 1912, and in 1924 was elected (the only Italian) an Honorary Member of that body. He was a member of many other scientific societies and academies, as well as a member of the Board of Directors and Chairman of the Patent Committee of International Latex Processes Limited.

Bruni's participation in the public life of his country (he was a member of Parliament from 1929 on and was nominated Senator by the King early in 1943) was to end in sheer bitterness because, owing to his awareness and acute sense of responsibility, he foresaw the outcome of many absurdities he was witnessing but was unable to avail against them because his spirit of tolerance and moderation went unheeded in that tragic period. When the dictatorship collapsed in July,

1943, soon to be followed by the collapse of the monarchy, Bruni retired to strictly private life, but the writer received many demonstrations of his sympathy for the new birth of democracy in his country. Bruni's last concern and last working effort in the summer of 1945 were for his book, a treatise on general and inorganic chemistry for student use. In the foreword of the last edition, Bruni had written:

I give this book to the printer not without emotion because, thus enlarged and completed, it represents my scientific legacy.

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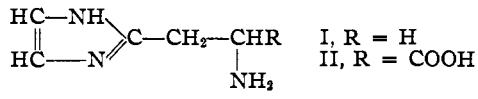
[CONTRIBUTION FROM THE LILLY RESEARCH LABORATORIES]

Studies on Imidazole Compounds. I. A Synthesis of Imidazoles with Functional Groups in the 2-Position

BY REUBEN G. JONES

In connection with a broad study of possible relationships of chemical structure to biological activity, it was of interest to prepare the isomer (I) of histamine and the isomer (II) of histidine in which the side chains were attached to the 2-position of the imidazole nucleus.



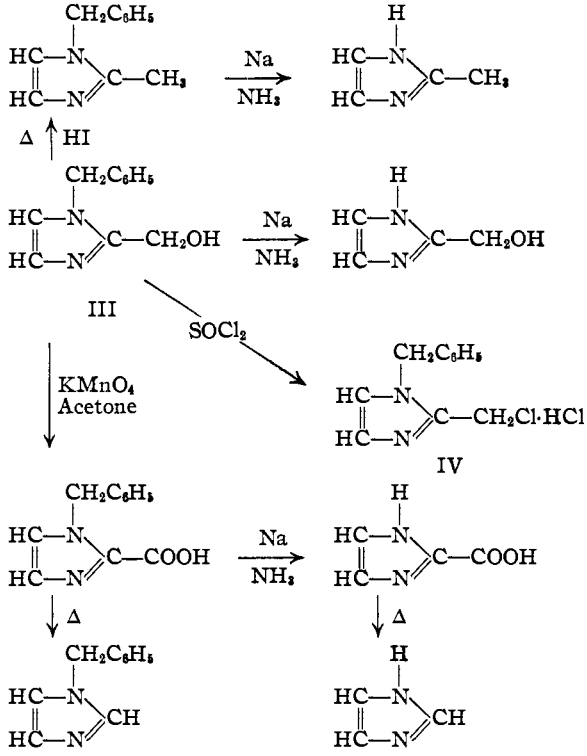
I, R = H
II, R = COOH

These compounds have been synthesized by a method which appears to be generally applicable to the preparation of a variety of 2-substituted imidazoles. A number of other new members of this little-known class of compounds are also reported at this time.

It has been shown[1a,b,c] that certain imidazoles having a methyl group in the 1-position will condense with formaldehyde to yield the corresponding 2-hydroxymethylimidazoles. These compounds can then be converted to a variety of other derivatives.[1b] In the present investigation 1-benzylimidazole has been used as the starting material. When heated with an excess of aqueous formaldehyde, 1-benzylimidazole gave an almost quantitative yield of 1-benzyl-2-hydroxymethylimidazole (III) which was isolated easily as the crystalline hydrochloride. Proof that the hydroxymethyl group entered the 2-position was provided by hydriodic acid reduction of the compound to yield 1-benzyl-2-methylimidazole. This was dissolved in liquid ammonia and treated with sodium to remove the benzyl group according to the method of du Vigneaud and Behrens.[2] The known 2-methylimidazole was thus obtained. It was found that in general these 1-benzylimidazoles are easily debenzylated by the sodium–liquid ammonia method. On the other hand one attempt to cleave the benzyl group by catalytic hydrogenolysis[3] did not meet with success.

(1) (a) Sarasin, *Helv. Chim. Acta*, **6**, 377 (1923). (b) Sonn, Hotes and Sieg, *Ber.*, **57**, 953 (1924). (c) Grindley and Pyman, *J. Chem. Soc.*, 3128 (1927).
(2) du Vigneaud and Behrens, *J. Biol. Chem.*, **117**, 27 (1937).
(3) Cirkofer, *Ber.*, **75**, 429 (1942).

A number of transformations of 1-benzyl-2-hydroxymethylimidazole (III) are outlined in the reactions



For the synthesis of 2-β-aminoethylimidazole (I), 1-benzyl-2-chloromethylimidazole (IV) was converted to 1-benzyl-2-cyanomethylimidazole. This compound underwent smooth reduction with