

Professor C.D. Nenitzescu

A Tribute



IN MEMORIAM COSTIN D. NENITZESCU (1902-1970)

“Costin D. Nenitzescu belongs, like his teacher Hans Fisher, among the great architects of organic chemistry”
Rolf Huisgen

This Special Issue of *ARKIVOC* celebrates the 100th anniversary of the birth of Costin D. Nenitzescu, the founder of the Romanian school of modern organic chemistry.

As a former student and assistant of Professor Nenitzescu as well as the “facilitator” of this Commemorative Issue I will try to present briefly the personality and the main achievements of my Magister.

Costin D. Nenitzescu was born in Bucharest on July 15, 1902, the son of a lawyer, former minister for industry and commerce. After finishing the high school in Bucharest he began in 1920 the study of chemistry in ETH-Zurich, being deeply impressed by the courses of Hermann Staudinger and Peter Debye. Fascinated by the beautiful works of Hans Fisher (“the man who showed us why the grass is green and the blood is red”) he moved in 1922 to Munich where he continued and finished his studies in 1925 with a Ph.D. Thesis supervised by the master of porphyrin and pyrrole chemistry. Later Nenitzescu wrote: “From Hans Fisher I learned the trade secrets of being a research chemist; I learned from him how to pose a research problem, what one may and what one may not investigate, where to start and where to stop. I learned the tenacity which must accompany a research work. I learned that one must have the audacity to

attack difficult problems, even when they will take a long time and will require a substantial effort.”

On his return to Romania, Nenitzescu became professor of organic chemistry and general chemistry at the Bucharest University (1925-1935). In 1930 he obtained the title of *Dr.Habil.* In 1928, at the age of 26, he published simultaneously the first editions of what would later become his classical textbooks “Organic Chemistry” and “General Chemistry”. These manuals, the fundamental textbooks of more than 40 generations of Romanian students, were continuously improved and updated by the author in numerous successive editions (some of them translated into foreign languages).

Nenitzescu was a dedicated and illustrious teacher. He deeply impressed his students by presenting the beauty of organic chemistry in a very logical and captivating manner. Being extremely well informed in all domains of organic chemistry, and also in general, analytical and physical chemistry (he was a pioneer of application of physical methods in organic chemistry in Romania) he transmitted the knowledge in a calm, very clear and serene discourse. He did not hesitate to say to his students: “we don’t know yet”, “I don’t know”, “the mechanism is not elucidated” etc..... Nenitzescu strongly believed that “in order to succeed in transmitting science, one must create science or, at least, one must attempt to do so” (these words are now engraved along with his bronze effigy in the Bucharest Polytechnic Institute’s auditorium where he delivered his courses for 35 years. Nenitzescu also wrote: “I have always had the feeling that the most efficient way of restituting the benefits that are generously bestowed upon us by the society is by teaching”. “But why seek such categorical imperatives? I simply love my job of teacher and, as we all know, one can give only what he has.”

Nenitzescu was elected as a corresponding member of the Romanian Academy in 1945 and as a full-member in 1955. His increasing international recognition has as effect his election as a member of several foreign Academies of Science (Germany, Soviet Union, Czechoslovakia, Hungary, Poland). Professor Nenitzescu’s name is also connected with the organization, development and leading of chemical research institutions in Romania. Starting in 1947 he directed a research unit of the Ministry of Chemical Industry and in 1964 he was the founder of the Research Center for Organic Chemistry of the Romanian Academy, whose director and illustrious animator he remained until his death. He was also the Editor in Chief of *Revue Roumaine de Chimie* and of other chemical journals published by the Romanian Academy.

He was married to his co-worker, Professor Ecaterina Cioranescu (1909-2000), the first woman assistant in the Department of Organic Chemistry, later also member of the Romanian Academy. About her, Professor P.F.G. Praill wrote, in a memorial tribute to CDN: “...his wife, who ably but unobtrusively supported him in his scientific work, has the sympathy of chemists from many lands”.

The notable results of the scientific activity of Professor Nenitzescu were published in 262 original papers and 21 patents. The main research domains and some selected main original achievements are noted below:

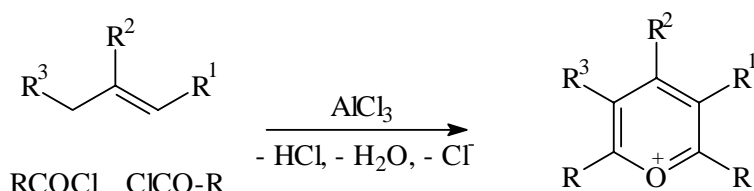
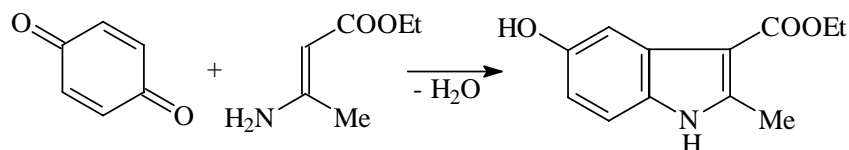
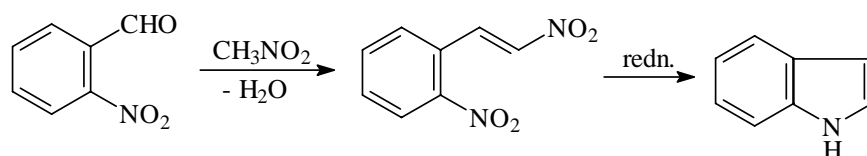
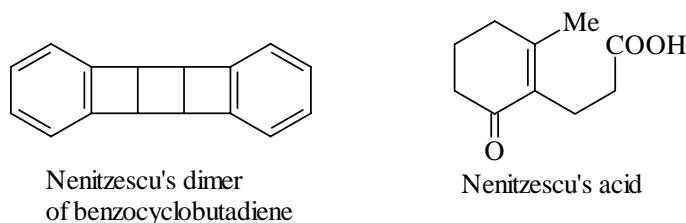
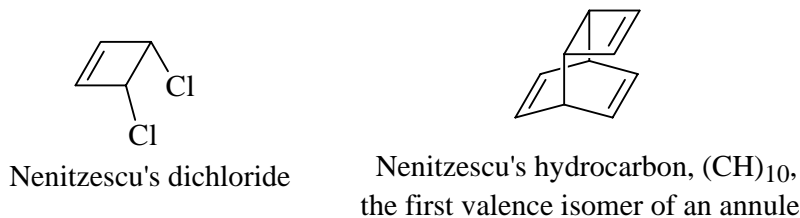
1. *Investigations in pyrrole and indole series* – two new syntheses bearing his name – *vide infra*, syntheses of degradation products of the blood pigments.

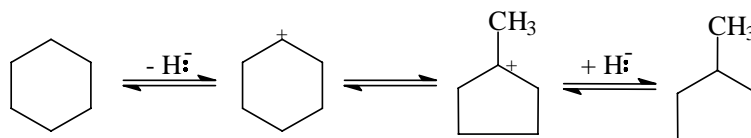
2. *Nitro derivatives and acinitro derivatives* – dimerization of acinitro derivatives, thermal reactions of iodo-nitro derivatives, mechanism of conversion of acinitro derivatives into hydroxamic acids.
3. *Romanian oil* – isolation of cycloalkanic acids, prehnitol, 1,6- and 2,6-dimethylnaphthalenes from Romanian oil, convergence of the melting points series of normal paraffins.
4. *AlCl₃-catalyzed reactions* – isomerizations of alkanes and cycloalkanes in the presence of AlCl₃, mechanism of isomerization including hydride ions, halogen migrations in acyclic and cyclic chains, isomerization of phenylalkanes, alkylations and acylations of alkanes and cycloalkanes, reductive acylation of alkenes, reaction of alkanes and cycloalkanes with carbon monoxide, mechanism of the Scholl reaction, two chapters (together with A.T. Balaban), “Dehydrogenation-Condensation of Aromatics” and “Aliphatic Acylation”, in the well-known “Friedel-Crafts and Related Reactions” of G.A. Olah.
5. *Pyrylium salts* – a new method of synthesis *via* diacylation of olefins, structure and reactions of pyrylium salts.
6. *Mechanism of aromatic alkylation* – kinetics of alkylation with arylsulfonates, ebulliometric study of benzene-sulfonic acid association, general mechanism of the Friedel-Crafts alkylation.
7. *Cyclobutadiene, cyclooctatetraene and valence isomers of annulenes* – synthesis of *cis*- and *trans*-dimers of cyclobutadiene, synthesis of the linear dimer of benzocyclobutadiene, syntheses with cyclooctatetraene leading to the first valence isomer of an annulene, (CH)₁₀ – *vide infra*, substituted benzocyclobutadienes, reactions of acetylenes with transitional metals, 1,2-dichlorocyclobutene (Nenitzescu’s dichloride) – *vide infra*; investigation of cyclobutanecarboxylic acids.
8. *Carbenium ion reactions* – stereospecific reversible carbenium ion rearrangements in the dihydroanthracene and dihydrophenanthrene derivatives, retro- π -route in solvolysis reactions, two excellent chapters (“Historical Outlook” and “Intermolecular Hydride Transfer Reactions involving Carbenium Ions”) in Olah and Schleyer’s well-known monograph “Carbenium Ions”.
9. *Oxidations* – mechanism of the Etard oxidations of hydrocarbons and epoxides.
10. *Additions and eliminations* – solvolytic halogen additions to olefins in ethereal solvents, eliminations of elemental bromine through bromide ions, kinetics of bromine eliminations, steric effects in elimination.

The essential, highly original contributions of Nenitzescu’s works were and continue to be recognized, appreciated and quoted in the international chemical literature. For example, in the ’70s an empirical enumeration of these quotations exceeded 1000, and even today, 30 years after his death, the Chemistry Citation Index usually counts more than 20 Nenitzescu’s quotations yearly. Other examples include *e.g.*: a) the printed text of the first page from “Friedel-Crafts alkylation chemistry. A century of discovery” by R.M. Roberts and A.A. Khalaf, (M. Dekker, 1984): “This book is dedicated to Professors Costin D. Nenitzescu and Ecaterina Cioranescu–Nenitzescu with appreciation and affection”; b) the opinion of E. Vedejs concerning the mechanism (a very controversial one) of pyrolysis of Nenitzescu’s hydrocarbon: “In their first paper on (CH)₁₀ structures, Nenitzescu and co-workers proposed a highly intuitive rationale for

rearrangement which was in fact based on the intermediacy of tricyclo[4.4.0.0^{2,5}]decatriene. These papers precede the revelation of orbital symmetry concepts by several years..."; c) different other appreciations enunciated by a multitude of organic chemists of the time (H. Fisher, R. Criegee, G. Wittig, K. Hafner, G. Schroder, E. Vogel, A. Dreiding, E.O. Fischer, O.A. Reutov, R. Hoffman, G.A. Olah, S. Winstein, P.v.R. Schleyer, V. Prelog, R. Huisgen, S.J. Cristol, A. Butenandt, K. Winnacker and many others (see also below).

Because a more detailed description of the original works of Costin D. Nenitzescu is beyond the scope of this foreword, in the following scheme only the reactions and compounds bearing his name in the international chemical literature will be collected:





The Bartlett-Nenitzescu-Schmerling hydride shift in the acid-catalyzed isomerization of cycloalkanes and alkanes

Scheme 1

Nenitzescu was a tenacious researcher, never discouraged by unsuccessful attempts; he often used to quote Fridtjof Nansen's words: "Have you not succeeded? – Continue! – Have you succeeded? – Continue!". Numerous chemists in Romania and abroad admired him for his audacity, for always attempting new exciting research domains, under modest material conditions. Thus, after his well-known achievements in AlCl_3 -catalyzed reactions, mainly performed in his youth, he tackled at the age of 50 the investigations of cyclobutadiene and valence isomerism, at the age of 60 he started the investigations of carbenium ions, at the age of over 60 he began the investigation of oxidation reactions and elimination reactions and so on.

Costin Nenitzescu had also notable achievements in the Romanian chemical technology, starting with the first Romanian pilot-plant of synthetic rubber (in 1942-43), technological processes for drugs and pesticides and going up to semi-industrial fabrication – independent of Ziegler's researches - of a new type of polyethylene, the so-called "AS-polyethylene" (from amyl-sodium). He was distinguished with numerous Romanian and foreign medals, orders and prizes including the prestigious August Wilhelm von Hofmann gold medal of the Gesellschaft Deutscher Chemiker. In 1968 he achieved a famous success as Max Tishler Lecturer in USA, as attested *e.g.* by Paul Bartlett ("your lecture at Harvard was the high point of the year"), Konrad Bloch ("...the great treat that you gave us with your visit. Not only did all of us enjoy your beautiful lecture, but we were exceptionally fortunate to get to know Professor Nenitzescu, the man, as well as the scholar"), S. Winstein and many others.

Nenitzescu had an unusual gift of intuition about the qualities of his students, selecting practically without failure the best of them as his future co-workers. He perfectly managed also the art of using, with a maximum yield, the specific qualities of each co-worker, succeeding thus to create an integrated viable research school, well recognized in Romania and abroad. It is worthwhile to remember here the opinion of Professor Rudolf Criegee that the research students who came from Nenitzescu's school were the best trained and the most productive students in the Karlsruhe's laboratories.

Nenitzescu was also a *great man*. Though apparently a very austere person he was very warm-hearted and generous. He passionately loved the high mountains where he often led the whole group of co-workers in unforgettable trips. He loved history (especially of ancient times), art (impressionists) and classical literature (Goethe, Shakespeare).

Before closing this presentation, a few comments about Nenitzescu by some well-known contemporary chemists will be mentioned:

"Costin Nenitzescu – an outstanding but never fully recognized Romanian chemist – carried out much pioneering research on acid-catalyzed reactions...Leading investigators such as P.D. Bartlett, C.D. Nenitzescu, S. Winstein, D.J. Cram, M.J.S. Dewar, J.D. Roberts, P.v.R. Schleyer

and others – have contributed fundamentally to the development of modern carbocation chemistry.” (George A. Olah - Nobel Lecture, 1994)

“Your achievements in chemistry impress me very much, when I think that you succeeded to do this far from the great chemical centers, and lacking modern instrumentation. Hans Fisher, our common professor, would have enjoyed your work, seeing how you looked for other areas of research than those you became familiar with, during your Ph.D. studies.” (Professor H. Plieninger, Heidelberg)

“In particular, it was especially stimulating for me to meet you because I had come over the years to recognize and appreciate your splendid professional work in chemistry.” (Professor H. Gilman, Iowa State University)

“We have memories of friendly, serious, hard-working, warm-hearted people whom we will never forget... It was a satisfaction for me to discover how organic chemistry should be developed to such a high state in a small far-away country, which so few of us ever visited. Now I know what I should have guessed, that the enthusiasm and strength of one man was behind it. I feel inspired and enriched in my own life for having been exposed to him, if only for a few days. It is indeed a very rich man who can look on a life of rich and lasting contributions and a family of students prepared to extend the tradition into the future without limit.” (Professor W.v.E. Doering, Harvard University, after his first visit to Romania in 1970)

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The author of this foreword expresses his highest appreciation to Professor Alan R. Katritzky, *Dr. honoris causa* of Polytechnic University Bucharest, a friend of Professor Nenitzescu, for approving and making possible the publication of this Anniversary Issue of *ARKIVOC*, for nominating me as the “facilitator” and for all his help and understanding. My special thanks are addressed also to Dr. A. John Boulton, the Coordinating Editor of *ARKIVOC*, an old friend of Romanian chemists, as well as to Professor Mikael Begtrup, the Scientific Editor, for their steady interest and help in editing this Issue.

My respectful thanks are directed also to Professor George A. Olah and his co-workers, who without any hesitation and delay sent a special contribution to this Anniversary Issue, as well as to all Romanian authors (most of them former distinguished co-workers and/or students of Costin Nenitzescu) who agreed to help us in the production of this celebratory issue dedicated to the memory of the *MAGISTER* of Romanian Organic Chemistry.

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