SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY
SOUTH. BRAZ. J. CHEM., Vol. 10 , N° 11, 2002

COSTIN D. NENITZESCU (1902 -1970) 100 th ANNIVERSARY OF HIS BIRTH

Lavinel G. Ionescu
Departamento de Química Pura, Faculdade de Química
Pontifícia Universidade Católica do Rio Grande do Sul - PUCRS
Porto Alegre, RS BRASIL 90610-900
&
Departamento de Química, Faculdade de Ciências Naturais e Exatas
Universidade Luterana do Brasil - ULBRA
Canoas, RS BRASIL 92420-280

ABSTRACT

Costin D. Nenitzescu was born in Bucharest in 1902 and passed away in Busteni, Romania in 1970. He obtained primary and secondary education in Romania and began university studies at the Swiss Federal Polytechnic Institute in Zürich. Later, he moved to the Technische Hochschule in München (Munich) where he worked with Hans Fischer and obtained the Doctor of Engineering Degree in 1925. During the same year he returned to Romania where he spent the rest of his life working, first at the University of Bucharest (1925-1935) and then at the Polytechnic Institute (1935-1970). Costin D. Nenitzescu is considered the founder of the School of Modern Organic Chemistry in Romania. He has published approximately 300 (three hundred) scientific articles, twenty books and treatises dealing mainly with organic chemistry and authored about forty patents. Several organic reactions bear his name. Costin D. Nenitzescu's work includes the chemistry of indole and pyrrole, Romanian petroleum, nitro-derivatives, reactions catalyzed by aluminum chloride, pyrylium salts, aromatic alkylation, cyclobutadiene, cyclooctatetraene, annulenes, carbonium ion reactions, eliminations, oxidations and additions.

KEYWORDS History of Chemistry. Aliphatic and Aromatic Alkylation. Nenitzescu Indole Synthesis. Naphthenic Acids. Mechanistic Organic Chemistry.

RESUMO

Costin D. Nenitzescu nasceu em Bucareste em 1902 e faleceu em Busteni, Romênia em 1970. Fez os estudos primários e secundários na Romênia e começou os estudos universitários na Escola Politécnica Federal de Zurique. Mais tarde transferiu-se para a Technische Hochschule München (Munique) onde trabalhou com Hans Fischer o obteve o grau de Doutor em Engenharia em 1925. No mesmo ano voltou para Romênia, onde passou o resto de sua vida trabalhando, primeiramente na Universidade de Bucareste (1925-35) e depois na Escola Politécnica de Bucareste (1935-1970). Costin D. Nenitzescu é considerado o fundador da Escola Moderna de Química Orgânica na Romênia. Publicou aproximadamente 300 (trezentos) artigos científicos, aproximadamente vinte livros e tratados, principalmente sobre química orgânica e foi o inventor de aproximadamente quarenta patentes. Várias reações orgânicas levam seu nome. O trabalho de Costin D. Nenitzescu inclui a química do indol e pirol, petróleo romeno, nitroderivados, reações catalizadas por cloreto de alumínio, sais de pirílio, alquilação aromática, ciclobutadieno, ciclooctatetraeno, anulenos, reações do íon carbônio, eliminações, oxidações e adições.

DOI: 10.48141/SBJCHEM.v10.n11.2002.4_2002.pdf

Costin D. Nenitescu (Nenitzescu in languages other than Romanian) was born in Bucharest on July 15, 1902 and passed away in Busteni, Romania on July 28, 1970.

He was a member of a prominent Romanian family from the Galati Region. His uncle , Ioan Nenitescu (1854-1901) studied at the University of Iasi and in Germany, was mayor of Tulcea and a well known poet and patriot. His father, Dimitrie Nenitescu (1865-1930) followed a military career, later studied law at the University of Louvain, Belgium and published an important work entitled *"The Danube and International Law"*. As Minister of Industry and Commerce he was fundamental in the promulgation of the first law dealing with workers insurance, benefits, social security and regulation of professions in Romanis.

Costin D. Nenitzescu received a very good primary and secondary education and graduated from the *Gh. Lazar Lyceum*, the most prestigious secondary school in Bucharest. In the fall of 1920 he travelled to Switzerland and enrolled as a student at the Swiss Federal Polytechnic Institute in Zürich. Among his teachers in Zürich were Peter Debye *(Nobel Prize 1936)* and Hermann Staudinger *(Nobel Prize 1953)*. In 1922, Costin D. Nenitzescu moved to Munich to study with Hans Fischer, a chemist, physician and biochemist at the Technische Hochschule. He was fascinated by Hans Fischer's work with blood, bile and leaf pigments. Munich, at the time could be considered one of the world's centers for organic chemistry with Richard Willstätter (1872-1942;*Nobel Prize 1915*), Heinrich Wieland (1877-1957; *Nobel Prize 1927*) and Hans Fischer (1881-1945; *Nobel Prize 1930*).

He obtained the Doctor of Engineering Degree in 1925 and his thesis dealt with the synthesis of degradation products of blood pigments. During the same year he returned to Romania, where he spent the rest of his life working, first at the University of Bucharest (1925-1935) and then at the Polytechnic Institute of Bucharest (1935-1970).

Costin D. Nenitzescu is considered the Founder of the School of Modern Organic Chemistry in Romania. He has published approximately three hundred (300) scientific articles, twenty books or treatises dealing mainly with organic chemistry and authored about forty patents.

His research work includes indole and pyrrole derivatives, nitroderivatives, Romanian petroleum, reactions catalyzed by aluminum chloride, synthesis and reactions of pyrylium salts, mechanism of aromatic alkylation, cyclobutadiene, cyclooctatetraene, annulenes, carbonium ion reactions, eliminations, oxidations and additions. Several organic reactions bear his name.

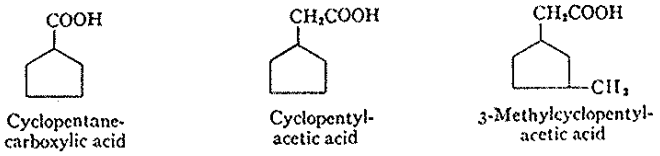
Costin D. Nenitzescu believed that applied research was an important part of the work of a scientist. His more than forty patents include industrial production of thiodiglycol, benzene, toluene, xylene, organic compounds of arsenic, polymerization of ethylene, chlorination of cyclohexane and

COSTIN D. NENITESCU (1902 – 1970)

benzene, production of chloroprene, terephthalate and bicycloheptadiene. He worked with nerve gases and was instrumental in the industrial production of many drugs in Romania during the difficult years following World War II.

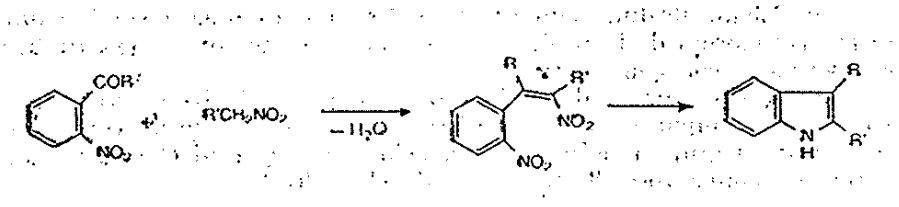
He held many positions in various agencies of the Ministry of Petroleum and Mines and the Ministry of Chemistry that dealt with industrial and technological development in Romania including INCT (Institutul National de Cercetari Tehnologice - 1947), ICEPS (Intreprinderile pentru Cercetari si Productie Semiindustriala - 1948), ICECHIM (Institutul de Cercetari Chimice - 1950) and IPROCHIM (Institutul de Proiectari Chimice - 1950).

Costin D. Nenitzescu studied the chemistry of coal from the Petrosani Region, but a more important contribution was the discovery and isolation of several naphthenic acids, tetramethylbenzene and dimethylnaphthalenes in Romaniam petroleum. Naphthenic acids have many technical uses, including mildew proofing of sandbags, rope for use at sea, wood, cotton, jute and hemp, compounding of special lubricants for high pressure and NAPALM, employed widely for incendiary bombs.



SOME OF THE NAPHTHENIC ACIDS DISCOVERED BY COSTIN D. NENITZESCU IN ROMANIAN PETROLEUM.

Several organic reactions were named after Costin D. Nenitzescu. In 1925 he published in *Berichte der Deutschen Chemischen Gesellschaft* a new reaction for the synthesis of indole (Nenitzescu Indole Synthesis).

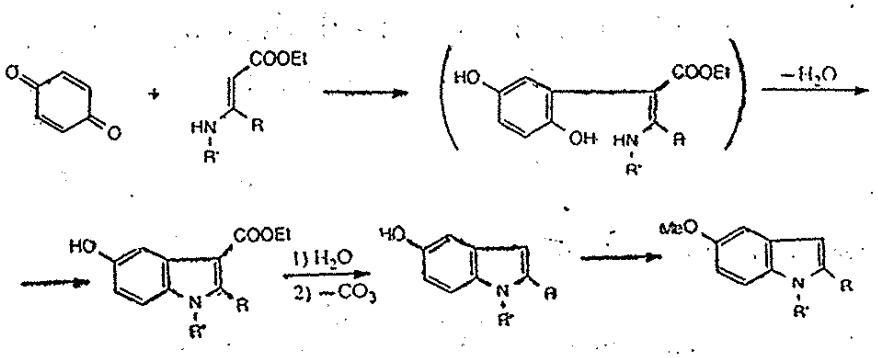


NENITZESCU INDOLE SYNTHESIS.

AUGUST WILHELM VON HOFMANN GOLD MEDAL AWARDED BY THE GERMAN CHEMICAL SOCIETY.

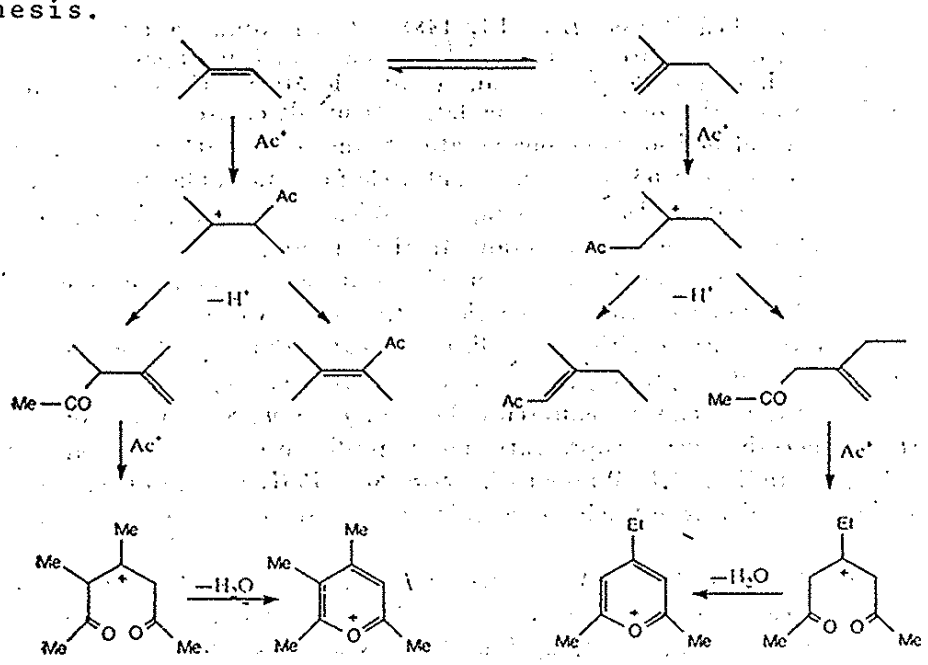
ROMANIAN POSTAGE STAMPS HONORING C.D. NENITESCU

Four years later he developed an improved synthesis for 5-hydroxyindole (*Cf. Bull. Soc. Chim. Rom.,11,37, 1929*). Both reactions are still widely used today to obtain biologically active compounds. The second reaction is more important and is used to prepare tryptamine, serotonin and indoleacetic acid.



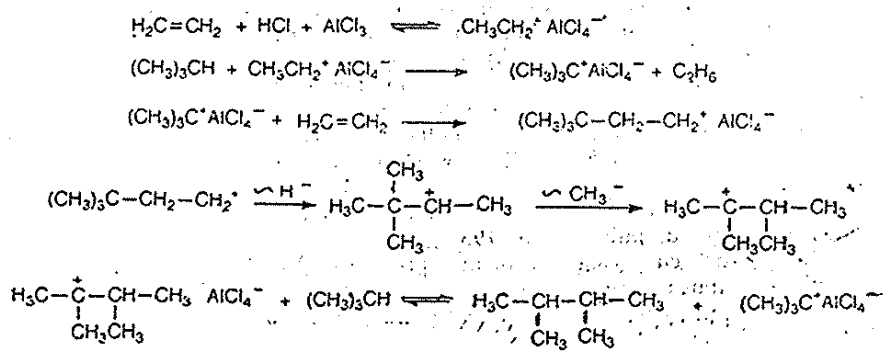
NENITZESCU 5-HYDROXYINDOLE SYNTHESIS.

The work of C.D. Nenitzescu and A.T. Balaban on the synthesis of pyrylium salts was published simultaneously with P.F.G. Praill of Queen Elizabeth College, London (*Cf. J. Chem. Soc.,1961,3553-3573*) and the reaction is generally known as the Balaban-Nenitzescu-Praill Pyrylium Salts Synthesis.



BALABAN-NENITZESCU-PRAILL PYRYLIUM SALTS SYNTHESIS.

Hydride Transfer Reactions during Friedel-Crafts Catalysis were studied by Nenitzescu and his collaborators during War War II and were first described in 1945 (*Cf. Acad. Roum. Bull. Section Scientifique, XXVII (10),1, 1945*). Today this reaction is known as the Bartlett-Nenitzescu-Schmerling Migration.



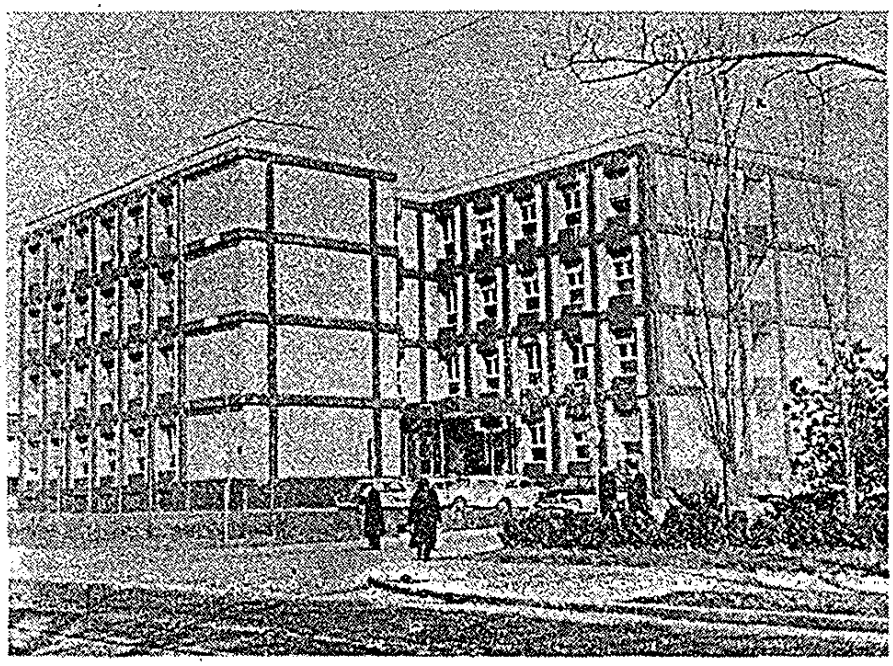
BARTLETT-NENITZESCU-SCHMERLING MIGRATION.

Costin D. Nenitzescu has published more than twenty books at all levels, dealing mostly with organic chemistry, but including topics such as nerve gases, technical dictionaries in many languages and chemical engineering. His book on advanced organic chemistry was translated to many languages.

He was a member of many scientific societies and received many prizes and awards. Among them we cite the *August Wilhelm vonHofmann Gold Medal*, the highest award of the German Chemical Society. He was distinguished by Scientific Academies in Romania, Germany, Russia, Poland, Czechoslovakia and Hungary.

We met Professor Nenitzescu and his wife Ecaterina Cioranescu-Nenitzescu in Bucharest in 1965. At the time we visited him at his home on Strada Scoalei. As a young, aspiring chemist we presented him with a copy of our Master's Thesis on Liquid Scintillators, work done at the University of New Mexico and the Los Alamos Scientific Laboratory under the supervision of G.H. Daub and F. Newton Hayes. Costin D. Nenitzescu was a kind, warm hearted person. He had a noble bearing and implied respect. We remember a large desk in his study full of books on organic chemistry. We recognized most of the treatises and manuals that were in use in the United States.

At the time, one of Costin D. Nenitzescu's major preoccupations was the construction of the new Research Center of Organic Chemistry of the Romanian Academy. It was eventually inaugurated in 1968 and it still functions today.



NEW BUILDING OF THE CENTER OF ORGANIC CHEMISTRY IN BUCHAREST INAUGURATED IN 1968.

One of his best friends was Horia Hulubei, a Romanian physicist and co-discoverer of francium. They served together on many scientific commisions and both enjoyed mountain climbing in the Carpathians around Sinaia and Busteni.

Costin D. Nenitzescu firmly believed in the importance of resaerch. He was convinced that the person that transmits science must be a researcher, a creator of science, or at least should try to be one. Some of his former students are today renowned scientists working in Romania, United States, Germany, Moldavia, Israel and other countries.

He was preoccupied with both pure and applied research. In fact, his last address before the Academy of Science of the Socialist Republic of Romania in July 1970, a few weeks before his death, was entitled *"Meditations on the Relation between Science and Technology"*. Costin D. Nenitzescu thought that both pure and applied research were important. His thinking was based on the analysis of science and technology from antiquity to the present time and on the role that scientists played throughout history. According to him, activity in science should never be directed or controlled. In fact, liberty or the freedom to search the truth is the most important aspect of science.

Some representative publications of Costin D. Nenitzescu (after ref. 1) are listed on the following pages.

SOME REPRESENTATIVE PUBLICATIONS (After reference 1):

1924 1. H. Fischer und C. D. Nenitzescu, Synthesen der Phyllopyrrol-carbonsäure, *Liebigs Ann. Chem.*, **439**, 175 (1924).

1925 2. H. Fischer und C. D. Nenitzescu, Einwirkung von Formaldehyd und von substituierten Alkoholen auf Pyrrolderivate und eine neue Synthese der Kryptopyrrol-carbonsäure, *Liebigs Ann. Chem.*, **443**, 113 (1925).

3. H. Fischer und C. D. Nenitzescu, Synthese der carboxylierten Kryptopyrrol-carbonsäure und einiger Methene, zugleich ein Beitrag zur Kenntnis der Ehrlichschen Dimethyl-amido-benzaldehydreaktion, *Hoppe-Seyler's Z. physiol. Chem.*, **145**, 295 (1925).

4. C. D. Nenitzescu, Über eine neue Indol-Synthese, *Ber. dtsch. chem. Ges.*, **58**, 1063 (1925).

1926 5. C. D. Nenitzescu, Considération sur les configurations électroniques des combinaisons complexes, *Bul. Soc. Chim. Rom.*, **8**, 10 (1926).

1928 6. C. D. Nenitzescu, Dérivés du Bz-tétrahydro-Indol. Note Ière, *Bul. Soc. Chim. Rom.*, **10**, 131 (1928).

7. C. D. Nenitzescu et V. Scortzeanu, Dérivés du Bz-tétrahydro-indol. Note II-me, *Bul. Soc. Chim. Rom.*, **10**, 134 (1928).

8. C. D. Nenitzescu, Dérivés du Bz-tetrahydro-indol. Note III-me, *Bul. Soc. Chim. Rom.*, **10**, 141 (1928).

9. S. Minovici, C. D. Nenitzescu et B. Angelescu, Sur quelques dérivés du 2.5-diphenyl-oxazole, *Bul. Soc. Chim. Rom.*, **10**, 149 (1928).

1929 10. C. D. Nenițescu, Contribuții experimentale la cunoașterea compușilor organici ai arsenului, folosiți ca gaze de luptă, *Revista Antigaz*, nr. 2—3, 1 (1929).

11. C. D. Nenițescu, Über einige Derivate des 2-Methyl-5-Oxy-indols, *Bul. Soc. Chim. Rom.*, **11**, 37 (1929).

12. C. D. Nenitzescu und D. Isăcescu, Über eine Abänderung der Gattermannschen Methode zur Darstellung von Phenol- und Pyrrol-aldehyden, *Bul. Soc. Chim. Rom.*, **11**, 135 (1929).

13. C. D. Nenitzescu, Über einige Umsetzungen der Magnesyl-Pyrrole und Indole, *Bul. Soc. Chim. Rom.*, **11**, 130 (1929).

14. C. D. Nenitzescu, Über die Einwirkung von Iod auf *aci*-Nitro-alkali-Verbindungen, *Ber. dtsch. chem. Ges.*, **62**, 2669 (1929).

1930 15. C. D. Nenițescu, C. N. de Bie și I. Cantuniari, Arbanita. Cloro-cetone aromatice din petrolul românesc, *Revista Antigaz*, nr. 7—9, 1 (1930).

16. C. D. Nenitzescu und D. Isăcescu, Über die Einwirkung von Iod und von Halogen-Derivaten auf *aci*-Nitro-alkali-Verbindungen, *Ber. dtsch. chem. Ges.*, **63**, 2484 (1930).

17. C. D. Nenitzescu, Le mécanisme de l'action des composés organo-magnésiens sur les amides N-disubstituées des acides α, β-non saturés, *Bul. Soc. Chim. Rom.*, **12**, 48 (1930).

1931 18. C. D. Nenitzescu und D. Isăcescu, Über die Einwirkung von Reduktionsmitteln auf Iod-nitro-Verbindugen. III. Mitteilung, *Bul. Soc. Chim. Rom.*, **13**, 89 (1931).

19. C. D. Nenitzescu und C. N. Ionescu, Durch Metall-halogenide katalysierte Reaktionen. I. Über die Einwirkung von Aluminiumchlorid auf Halogenverbindungen in Gegenwart von Cycloparaffinen, *Liebigs Ann. Chem.*, **491**, 189 (1931).

20. C. D. Nenitzescu, D. Isăcescu und C. N. Ionescu, Durch Metall-halogenide katalysierte Reaktionen. II. Über den Mechanismus der Friedel-Craftsschen Reaktion, *Liebigs Ann. Chem.*, **491**, 210 (1931).

21. C. D. Nenitzescu und E. Solomonica, Über die Einwirkung von aliphatischen Diazoverbindungen auf Pyrrol und seine Homologen, *Ber. dtsch. chem. Ges.*, **64**, 1942 (1931).

1942 68. C. D. Nenitzescu und E. Ciorănescu, Durch Aluminiumchlorid katalysierte Reaktionen. XXIII. Mitteilung. Versuche zur Synthese von Verbindungen mit Steringerüst, *Ber. dtsch. chem. Ges.*, **75**, 1765 (1942).

1944 69. C. D. Nenitzescu and V. Vântu, Mesomerism and Substitution in Aromatic Compounds, *Acad. Roum. Bull. section scientifique*, XXVII (4), 1 (1944); *Ber. dtsch. chem. Ges.*, **77**, 705 (1944) (Ger.).

1945 70. C. D. Nenitzescu, Über die Aluminiumchlorid-Katalyse auf dem Gebiete nichtaromatischer Verbindungen, *Acad. Roum. Bull. section scientifique*, XXVII (10), 1 (1945).

1961 147. A. T. Balaban and C. D. Nenitzescu, Pyrylium Salts Obtained by Diacylation of Olefins. Part. II. The two Pyrylium Salts Formed in Diacetylation of 2-Methylbut-2-ene, *J. Chem. Soc.*, **1961**, 3555.

148. A. T. Balaban and C. D. Nenitzescu, Pyrylium Salts Obtained by Diacylation of Olefins. Part III. Diacylation of Cyclic Olefins and a Novel Synthesis of Isoquinoline Derivatives, *J. Chem. Soc.*, **1961**, 3561.

149. A. T. Balaban, C. D. Nenitzescu, M. Gavăt and G. D. Mateescu, Pyrylium Salts Obtained by Diacylation of Olefins. Part IV. Di- and Tri-acetylation of Allyl-benzene, *J. Chem. Soc.*, **1961**, 3564.

150. A. T. Balaban and C. D. Nenitzescu, Reaction of Pyrylium Salts with Alkali Cyanides, *J. Chem. Soc.*, **1961**, 3566.

151. C. D. Nenitzescu et A. Glatz, Migration d'ions hydrure en des chaines d'acides éthyléniques au cours de la réaction de Friedel et Crafts, *Bull. Soc. chim. France*, **1961**, 218.

152. M. Avram, G. D. Mateescu, I. G. Dinulescu, E. Marica and C. D. Nenitzescu, A Dimer of Cyclobutadiene, *Tetrahedron Letters*, **1961**, nr. 1, 21.

1969 229. M. Avram, G. D. Mateescu and C. D. Nenitzescu, Investigations in the Cyclobutane Series. XX. Stereoisomeric 1,2,3 4-Tetrabromocyclobutanes by the Hunsdiecker Reaction. *Rev. Roumaine Chim.*, **14**, 101 (1969).

230. E. Ciorănescu, A. Bucur, F. Badea, M. Rentea and C. D. Nenitzescu, Solvolytic π-Route to Dibenzobicyclo[2.2.2]octadiene and Dibenzobicyclo[3.2.1]octadiene Derivatives, *Tetrahedron Letters*, **1969**, 1867.

231. E. Ciorănescu, M. Banciu, R. Jelescu, M. Rentea, M. Elian and C. D. Nenitzescu, Acetolysis of 1:2,5:6-Dibenzocyclohepta-1,3,5-trienyl-7-ethyltosylate, *Tetrahedron Letters*, **1969**, 1871.

232. E. Ciorănescu, M. Bancin, R. Jelescu, M. Rentea, M. Elian and C. D. Nenitzescu, Carbonium Ion Reactions. V. Acetolysis of 1:2,5:6-Dibenzocyclohepta-1,3,5-trienyl-7-ethyl-β tosylate, *Rev. Roumaine Chim.*, **14**, 911 (1969).

233. M. Avram, I. G. Dinulescu, G. D. Mateescu, E. Avram und C. D. Nenitzescu, Untersuchungen in der Cyclobutanreihe. XXI. Di-*tert*-butyl-diphenyl-cyclobutadien Komplexe mit Palladiumchlorid, *Rev. Roumaine Chim.*, **14**, 1181 (1969).

234. M. Avram, I. G. Dinulescu, G. D. Mateescu und C. D. Nenitzescu, Untersuchungen in der Cyclobutanreihe. XXII. Ein Hexacarbomethoxy-Dewar-Benzol Komplex aus Acetylendicarbonsäure-dimethylester und Bis-benzonitrilpalladiumchlorid, *Rev. Roumaine Chim.*, **14**, 1191 (1969).

235. M. Avram, E. Avram, G. D. Mateescu, I. G. Dinulescu, F. Chiraleu und C. D. Nenitzescu, Untersuchungen in der Cyclobutanreihe. XXIII. Cyclisierende Trimerisierung von *tert*-Butylacetylen zu einem Dewar-Benzol-Palladiumchlorid Komplex, *Chem. Ber.*, **102**, 3996 (1969).

236. M. Avram, G. D. Mateescu, I. G. Dinulescu, and C. D. Nenitzescu, Untersuchungen in der Cyclobutanreihe. XXIV. Eine Umlagerung des Tricyclo [4.2.0.$0^{2,5}$] octan Systemes in das Tricyclo [4.2.0.$0^{2,4}$] octan System, *Chem. Ber.*, **102**, 4008 (1969).

237. M. Avram, I. Pogany, F. Badea, I. G. Dinulescu and C. D. Nenitzescu, Investigations in the Cyclobutane Series. XXV. The Addition of Bromine to 3,4-Benzotricyclo [4.2.1.$0^{2,5}$] nona-3,7-diene, *Tetrahedron Letters*, **1969**, 3851.

238. A. Ghenciulescu, I. Necşoiu, M. Rentea and C. D. Nenitzescu, The Étard Reaction. VIII. Oxidation of Diphenylethanes and Diphenylethylenes with Chromyl Chloride, *Rev. Roumaine Chim.*, **14**, 1543 (1969).

239. A. Ghenciulescu, I. Necşoiu and C. D. Nenitzescu, The Étard Reaction. IX. Oxidative Cleavage of Ethers produced by Chromyl Chloride, *Rev. Roumaine Chim.*, **14**, 1553 (1969).

240. V. Przemetchi, I. Necşoiu, M. Rentea and C. D. Nenitzescu, The Étard Reaction. X. Oxidation of Methylcyclopentane, Methylcyclopentene and of Methylenecycloalkanes C_5, C_6 and C with Chromyl Chloride, *Rev. Roumaine Chim.*, **14**, 1567 (1969).

241. M. Avram, D. Constantinescu, I. G. Dinulescu and C. D. Nenitzescu, Investigations in the Cyclobutane Series. XXVI. Attempted Synthesis of 1-*tert*.-Butylbenzocyclobutadiene and 1,2-Di-*tert*.-butyl-benzocyclobutadiene, *Tetrahedron Letters*, **1969**, 5215.

REFERENCES

1. M. Banciu and A.T. Balaban, "C.D. Nenitescu -Viata si Opera" (*C.D. Nenitzescu - Life and Scientific Work*), Editura Academiei Romane, Bucuresti, 1995, 255pp.
2. P. Karrer, "Kurzes Lehrbuch der Organischen Chemie", G. Thieme, Leipzig, 1933.
3. C. Ellis, "The Chemistry of Petroleum Derivatives", D. Van Nostrand, New York, 1934.
4. A. Streitwieser, "Molecular Orbital Theory for Organic Compounds", John Wiley, New York, 1962.
5. G.A. Olah, "Friedel-Crafts and Related Reactions", Interscience, New York, 1963.
6. J. March, "Advanced Organic Chemistry", John Wiley, New York, 1985.

ACKNOWLEDGEMENT. Special thanks are due to Prof. Dr. Cristina Mandravel, Chairperson, Department of Physical Chemistry, University of Bucharest for her help and assistance.

The SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY (ISSN: 2674-6891; 0104-5431) is an open-access journal since 1993. Journal DOI: 10.48141/SBJCHEM.
http://www.sbjchem.com.
This text was introduced in this file in 2021 for compliance reasons.
© The Author(s)
OPEN ACCESS. This article is licensed under a Creative Commons Attribution 4.0 (CC BY 4.0) International License , which permits use, sharing , adaptation , distribution , and reproduction in any medium or format , as long as you give appropriate credit to the original author (s) and the source , provide a link to the Creative Commons license , and indicate if changes were made. The images or other third-party material in this article are included in the article's Creative Commons license unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this license, visit http://creativecommons.org/ licenses/by/4.0/.