

## ACADEMICIAN DIMITER IVANOV

### 120 Years of His Birth



13.10.1894 – 25.10.1975

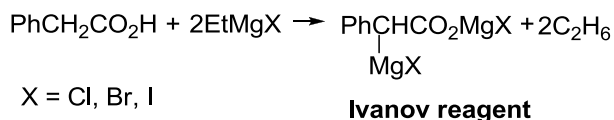
In the annals of Bulgarian science the name of Dimiter Ivanov holds a special place. In his fifty years of work he left ineffaceable and lasting traces in organic chemistry. His personal qualities and scientific achievements were on such a high international level that in him Bulgarian chemistry has one of its most outstanding representatives. The 120th anniversary of his birth is in October 2014.

Dimiter Ivanov Popov was born in the family of a clergyman on October 13 (27), 1894 in the village of Makotzevo in the district of Sofia. He graduated from the First High School for Boys in Sofia. He won a competition for a grant awarded by Stefan Beron from Kotel and in 1914 and 1915 he was studying chemical engineering in Lyon, France. On the declaration of mobilization in 1915, he returned to Bulgaria and took part in the First World War in Dobrudzha and Macedonia near Chervenata Stena. During the defeat of the Bulgarian army at Dobro Pole he was captured along with a Bulgarian army division near Thessaloniki and kept there up to the end of 1918.

He graduated in chemistry from Sofia University in 1920 and was immediately appointed as an assistant of Professor Zachary Karaoglanov in inorganic and analytical chemistry. Soon after that he obtained a grant to study in France again. He graduated as a chemical engineer in Nancy in 1922 with a Ph.D. degree and stayed for a year in the same university as a postdoc with G. Vavon, one of the outstanding stereochemists at that time. His first scientific paper on steric hindrance in catalytic hydrogenation dating from that time (1923) was published in *Comptes rendus de l'Académie des Sciences de Paris*.

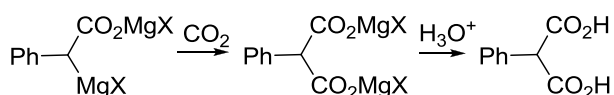
In 1926 Dimiter Ivanov became an Assistant Professor at the Chair of Organic Chemistry headed by Professor Pencho Raykov. The same year he obtained a Rockefeller Scholarship and went to work with Victor Grignard, a Nobel Prize winner who discovered the organomagnesium compounds. This was, to a great degree, the decisive factor in determining his further scientific career. Years afterwards Academician Ivanov would never forget and would emphasize to his students what he owed to this great man and scientist. Grignard welcomed his young Bulgarian colleague by handing over his own laboratory bench with the words "Here were discovered the magnesium reagents (known today as the Grignard reagents, author's remark) and I wish you with all my heart to move forward".

In 1931 Dimiter Ivanov, already an associate professor of organic chemistry in Sofia University, published a paper entitled "On a Method of Preparing Phenylmalonic Acid" in the *Bulletin de la Société Chimique de France*. Co-author of this work was his young Ph.D. student, later one of Bulgaria's great synthetic chemists Professor Alexander Spassov. Dimiter Ivanov had already published a dozen or more scientific communications abroad, but the above-mentioned paper laid the foundations of what is named today "*Ivanov reagents*" or "*Ivanov reaction*". Ivanov and Spassov reported that phenylacetic acid reacts with lower aliphatic Grignard reagents by liberating *ca.* two equivalents of hydrocarbon, for example:



**Ivanov reagent**

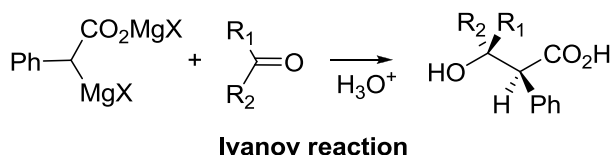
Phenylacetic acid thus behaves simultaneously as a carboxylic and as a C-H acid, i.e. a hydrogen atom of the methylene group can be replaced by metal. The organomagnesium compound so-obtained has a more complex structure than that of Grignard reagents but, to a considerable degree, possesses the reactivity of the latter. Different kinds of compounds give with the Ivanov reagent products which are either very hard or impossible to synthesize by other means. The first reaction of the newly obtained Ivanov reagent was carried out by the authors with carbon dioxide to yield phenylmalonic acid:



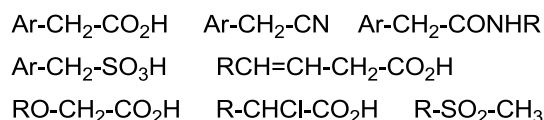
Thus a general method of preparing Ivanov reagents was set: metallation by means of Grignard reagents of compounds containing labile hydrogen atoms, called today C-H acids.

The same year D. Ivanov and A. Spassov discovered the reaction which would later be named the *Ivanov reaction*. It involves the interaction of the Ivanov reagents with aldehydes or ketones leading to  $\beta$ -hydroxy acids.

As recognition of this achievement next year, 1932, Dimiter Ivanov was awarded the honorary title of "Laureate of the French Academy of Sciences".

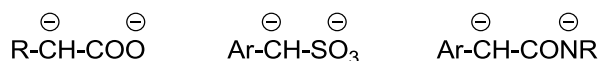


In the course of more than forty years Academician Ivanov worked steadfastly and systematically to develop the chemistry of organometallic compounds obtained by metalating C-H acids. After 1950, both in Bulgaria and abroad, there was a very intensive development of research along the perspectives outlined by Ivanov. Apart from magnesium, alkaline metals, zinc and calcium came into use and, in the case of each one, new features and fresh possibilities for application were found. The number of parent compounds which could be metalated was greatly expanded. The following are only a few examples:

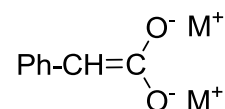


Dimiter Ivanov called the metal derivatives so-obtained "*polyfunctional organometallic reagents*". Already in the 'fifties outstanding scientists in USA, France, the USSR and other countries were introducing, using and substantiating the terms "*Ivanov reagents*", "*Ivanov-like reagents*", "*Ivanov reaction*".

Nowadays the concept of Ivanov reagents implies deprotonated derivatives of C-H acids, whose organic moiety, independently of the metal, may be considered as a two-charged anion capable to interact with one equivalent electrophile.



These reagents provide great synthetic opportunities because they are readily oxidized, alkylated, acylated and silylated, added to carbonyl and azomethine groups and conjugated double bonds. It was established that the formulas shown in the figure above, although easy to visualize, do not correspond to the real structure of Ivanov reagents. In some cases they are for example enediolates, as for the phenylacetic acid:



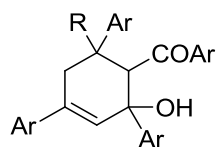
The reaction with carbonyl compounds named after Dimiter Ivanov belongs to the class of the so-called aldol reactions which are among the most important ones in organic chemistry. Many studies at home and abroad have clarified its similarities and differences with other aldol type reactions, such as Perkin, Reformatsky, Claisen. The kinetic stereoselectivity shows moderate degrees, *threo* diastereoisomer prevails, and depends on the metal and the solvent used. A mechanism of the reaction proposed by American scientists Zimmerman and Traxler, based on a six-membered transition state, explains the majority of the experimental data.

In experiments to react the Ivanov reagents with the unsaturated ketone dypnone an unexpected course occurred. It turned out that the product (no matter which organometallic reagent was used) was *dypnopinacone*, a class of *ca.* 60 compounds prepared and systematically studied by the great

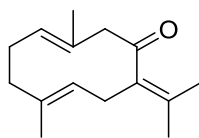
Belgian chemist Maurice Delacre. This was the beginning of another remarkable line of D. Ivanov's research. His first publications on this problem at the end of the 'thirties initiated a revision of the structure of dypnopinacones. Delacre himself, greatly impressed by the results obtained by his Bulgarian colleague with whom he had not been till then acquainted, sent Dimiter Ivanov his complete laboratory files. He wished Ivanov to bring to a successful conclusion the problem which had been his lifework. An extraordinary example of high moral behavior in the world of science!

In the 'forties, after having made use of a remarkable research strategy, Dimiter Ivanov and his then assistant Professor Tchavdar Ivanov disproved the structures suggested by Delacre and unequivocally determined the structure and mechanism of formation of dypnopinacones - a class of unsaturated cyclic hydroxy ketones. The brilliant solution to the dypnopinacone problem was the reason why dypnopinacone synthesis has been named "*Reaction of Delacre-Ivanov*".

The above examples are only a brief illustration of the impulse given to science by Academician Ivanov's research in the field of synthetic organic chemistry. This great scientist was not only a witness to its further useful development but also an active participant even in the last years of his life.



**Dypnopinacone**



**Germacrone**

In 1947 D. Ivanov took charge of a team of scientists who systematically investigated the composition of Bulgarian essential oils, above all rose oil, but also lavender, mint, sweet basil, zdravets (wild geranium) and the oil of other plants. The papers published became very widely known and contributed towards raising the international prestige of the products of the Bulgarian essential oil industry and the confidence in them. Academician Ivanov was welcomed everywhere as the "scientific ambassador" of the Kazanluk Oleaginous Rose.

The studies on zdravets oil, which is produced only in Bulgaria, deserve special attention. The crystal component of the oil, named *germacrone*, has a sesquiterpene carbon skeleton unknown in other natural compounds. In 1957 and 1958 a joint team of Bulgarian and Czech scientists, headed by

D. Ivanov and Fr. Šorm, proved germacrone to be a ten-membered ring ketone. This was the starting point for intensive research on various transformations on this structure, which contributed significantly to the prestige of the Bulgarian School of natural products chemistry.

Dimiter Ivanov published over 180 original scientific papers, some of them in Bulgarian journals but the greater part in foreign ones. In 1948 he was elected Corresponding Member of the Bulgarian Academy of Sciences and in 1961 Academician. Up to 1972 he was head of the "Organic Chemistry" section of the Chemical Institute of the Bulgarian Academy of Sciences, from the time of its foundation in 1951 (later this became "Laboratory of Organic Synthesis" to the Institute of Organic Chemistry).

The services rendered by Professor Dimiter Ivanov as a teacher and instructor were exceptional and indisputable. On the death of Professor Assen Zlatarov he was appointed (1937) to the Chair of Organic Chemistry at Sofia University, which he held up to 1962. His text-book on organic chemistry, which was excellent for that time, went through seven editions in the course of twenty five years. It has been the corner-stone in preparing many generations of chemists and chemical engineers. This text-book is now of great bibliographical value and today is still often used as a source of reference. Professor Ivanov had a profound feeling of responsibility and devotion in fulfilling his teaching duties. Having a marvelous memory he remembered everyone who had passed during decades through "his organic chemistry" and he always called them "our alumni". His lectures were unforgettable for many generations of students. Already in 1933 he was the initiator in introducing diploma works (master theses) which later became a well-established form for the instruction of students in most fields of study.

Academician Dimiter Ivanov stood out with his vivid and unique individuality. People's attitude towards his personality never was, and never could be, indifferent or indefinite. But everyone was, and is, unanimous in respect to his uncompromising attitude towards mediocre, opportunistic, lazy people, towards those who instead of serving science live on its back (these, to some extent, succeeded in avenging themselves on him when they provoked and caused his removal from the university in 1945 for one year, because of his "anti-people's behavior"). Nothing except personal qualities mattered to him in his estimation of people and his attitude towards them in general and towards his colleagues in particular. Maybe in this

lay the secret of his enviable insight in choosing his assistants and coworkers (never very many in numbers) and his approach in working with them. By creating a school in organic chemistry from which many of Bulgarian chemists started their career, Dimiter Ivanov raised a monument to himself already during his own lifetime.

He had a remarkable gift for getting in touch with people who were on most various professional and social levels. His inherent interest and curiosity about ordinary everyday problems made him a good listener and always good company. He would talk with equal satisfaction about his experiences with Nobel Prize winners or with some old neighbor in his native village of Makotzevo. It is easy to imagine him in lively conversation with students, or with the postman, or as the centre of attention at some scientific congress. This feature of his personality combined with his scientific and language culture made Academician Ivanov a desirable participant or guest at different international scientific meetings. The last event which he attended, still showing his youthful emotion, was the celebration of the centenary of the birth of Grignard in 1971. The Bulgarian scientist was invited to take part in it and was given the honor of delivering the speech on behalf of the

grateful former Grignard students, then scattered around many countries, whose indisputable doyen he was.

Academician Ivanov described his long career, illuminated by the rays of his sunset in his short "Memoirs", completed several weeks before he departed from us forever. The publication of these "Memoirs", unfortunately concealed by ill-wishers, would have provided not only an interesting, but also instructive reading matter. He passed away on October 25, 1975.

The absence of the personality of Dimiter Ivanov is very strongly felt at a time when the future of Bulgarian science is at stake! One always imagines that he would appear at the end of the corridor with his easy step and lively look, ready to tell us the next of his stories, to give us hope and faith in eternal values.

Blagoy Blagoev

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