IN MEMORIAM

YURII KONSTANTINOVITCH YUR'EV

(1896 - 1965)

Yurii Konstantinovitch Yur'ev, distinguished organic chemist, Doctor of Chemical Sciences, State Prize Laureate, and Moscow University Professor, died suddenly on 14 November 1965.

The death of this remarkable man and distinguished, erudite and talented teacher is a tragic loss to chemical science and to hundreds of his students, comrades, friends, and acquaintances. The loss is particularly tragic for this journal, on which he served as an active and learned editor.

Yurii Konstantinovitch Yur'ev was born at Saratov on 4 December 1896, in a working-class family. In 1915 he completed his secondary education in Moscow and entered the National Science Division of the Physicomathematical Faculty at Moscow University. He was called up in 1916 and his university studies were interrupted for almost two years. After demobilization in 1918, Yur'ev renewed his studies. However in the autumn of 1918 he enlisted in the Red Army and served on the Southern Front in 1919-1920. He returned to the University in 1923. In 1925 he graduated from the Chemical Division of the Physicomathematical Faculty at the Moscow State University and was awarded a Fellowship at the Zelinskii Laboratory.

In 1929 he was appointed Senior Assistant, in 1932 promoted to Reader, and in 1935 he was awarded a Master's Degree in Chemical Sciences.

In this period Yur'ev's activities were, to a large extent, centered on the study of the chemical composition of newly discovered oil deposits, the desulfuration of oil, and the cracking and isomerization of hydrocarbons under the action of $AlCl_3$. It was he who first applied the Zelinskii catalytic method of dehydrogenation for aromatic benzine and kerosene fractions and showed that this reaction has an industrial application in the production of aromatic hydrocarbons.

But already Yur'ev was interested in the chemistry of heterocyclic compounds, and this was to become his main field of research. Between 1927 and 1937 he achieved the catalytic dehydrogenation of thiophane, pyrrollidine and its M-substituents and the hydrogenation of pyrrole and its homologues.

In 1936 Yur'ev discovered the reciprocal conversion reaction of oxygen, sulfur, nitrogen, and selenium heterocyclic compounds. The conversion of furan into pyrrole, thiophene and selenophene was accomplished by passing the furan vapor with, respectively, NH_3, H_2S or H_2Se over Al_2O_3 at a high temperature. He also carried out reciprocal conversions on 5-ring heterocycles.

These reactions established for the first time a genetic link between different heterocyclic systems and showed the preferential direction of transformation from oxygen-containing heterocycles to rings containing other heteroatoms. He experimentally demonstrated the mechanism and limits of application of the reaction, the specific influence on it of different heteroatoms, ring dimensions, degree of substitution and also the quantity, position and characteristics of substituents.

On the basis of derivatives of furan (especially tetrahydrofuran) Yur'ev synthesized a large number of new nitrogen- and sulfur-containing heterocycles. In particular, the synthesis and detailed IR, UV and PMR spectral studies of numerous thiophene and pentamethylenesulfides were made possible by Yur'ev and his coworkers, who created the reliable standards essential for the identification of the cyclic sulfides present in sulfurous oils.

These important and orginal investigations led to wide chemical applications, both at home and abroad. The classical reciprocal conversion of heterocycles is now known as "Yur'ev's reaction" to modern students of organic chemistry. Currently, the Yur'ev reaction is used in industry to produce intermediates for the synthesis of various drugs.

In 1940 Yur'ev presented his brilliant Doctoral Dissertation, "Transformation of Oxygen-Containing Heterocycles into Rings with other Heteroatoms and into Hydrocarbons." In 1941 he was raised to the distinguished status of Professor. For his work in the field of heterocyclic chemistry, Yur'ev was awarded the Prize of the All-Union Mendeleev Society (1940), the Lomonosov Moscow University Prize (1944), and the State Prize of the USSR (1946).

In 1941-1943 Yur'ev established the Department of Organic Chemistry at the Sverdlovsk State University. In 1943 he returned to Moscow University where he was Professor in the Department of Organic Chemistry and acted as the chief specialist in the chemistry of heterocyclic compounds until the day of his death. For more than 20 years (1943-1964) Yur'ev was deputy to the head of the Department of Organic Chemistry Academician A. N. Nesmeganov.

His greatest scientific and pedagogic achievements followed World War II. He was the author of over 440 scientific papers, monographs, reviews, and educational texts.

To describe all of Yur'ev's wide and varied researches would be impossible, so I shall confine myself to a brief account of the main directions taken by his work in conjuction with his students and colleagues.

The chemistry of the simplest 5-membered heterocyclic systems, their fully hydrogenated analogues and derivatives represented the basis of Yur'ev's research. He developed general synthetic methods for many representatives of each class of substance and studied their characteristic properties.

The greater part of Yur'ev's work was concerned with the chemistry of derivatives of furan and tetrahydrofuran which he investigated exhaustively.

He studied in detail the reaction of furan and its homologues with unsaturated compounds. From the large number of examples chosen, he established rules for these reactions, i.e., whether the reaction proceeded by the diene synthesis or by substitution-addition. In particular, α, β-unsaturated carbonyl compounds react by substitution-addition and this serves as a convenient method for synthesizing ketones of the furan series with a carbonyl group in the gamma position of the side chain. This reaction path made the synthesis of trans-jasmone feasible.

Yur'ev used adducts of furan and its homologues with dienophiles, i.e., the systems 7-oxabicyclo [2, 2, 1] heptane, -hept-5-ene, and hepta-2, 5-diene, in extensive theoretical investigations on structural rearrangements and stereochemical addition reactions. He found in these systems that the Wagner-Meerwein rearrangement proceeded with the formation of alkoxy, acyloxy or halogen derivatives of 2-oxabicyclo [2, 2, 2] heptane. Thus the chemical path of the reaction (e.g., the formation of dinitrophenylhydrazones) proves that rearrangement has occurred. He established that exo-cis-addition occurs at the double bond in the system 7-oxabicyclo- [2, 2, 1] heptane. For example, hydroxymercuration of these compounds was feasible, and detailed development of the method established the configuration of the β-hydroxymercurized alcohols which were formed.

The halogenomethyl- and bis (halogenomethyl) furans also showed considerable synthetic potentialities. He studied their reactions with many nucleophilic reagents, paying special attention to the synthesis of numerous examples of mono- and diamines of the furan series. Among the latter were amines with significant pharmacological activity.

Yur'ev was the first person to accomplish the allyl-type rearrangement in halogenmethylfurans, substituted in position 5. For example, he prepared 2-methylene-5-chloromethyl-2, 5-dihydro-5-furonitrile from 2, 5-bis (chloromethyl) furan. The 2, 6-dimethylpyrone was formed by reduction and hydrolysis of the former.

He showed that 3, 4-bis (chloromethyl) furan is a convenient starting substance for the synthesis of the condensed structures of 3H-thieno- [3, 4-c] furan and 3H-dihydropyrolle (3, 4-c) furan.

Starting with 2, 5-bis (chloromethyl) furan, he achieved the synthesis of furan-2, 5-dialdehyde and he studied its condensation reaction in detail. By kinetic methods, he showed that the chlorine atom in 2-chloromethylfuran was very labile compared with the 3-isomer. This was also true for 2, 5-bis (chloromethyl) furan compared with the analogous 3, 4 derivative.

Yur'ev studied ketones and diketones of the tetrahydrofuran series, furanid-3-ones and furamidine-3, 4-diones, for many years. The development of original synthetic methods, detailed study of their structures and a multiplicity of reactions with electrophilic compounds led to the use of furanid-3-ones and furanidin-3, 4-diones in ring expansion reactions (transformation to compounds of the tetrahydropyran series and ring contraction production of ethoxy carboxylic acids). These methods were also used for the synthesis of bi- and tricyclic systems, containing pyrazole, imidazole, quinolinic, pyrazine, benzopyrillic, etc (in addition to tetrahydrofuran) rings.

In a long series of experiments, Yur'ev discovered and studied in detail a new method for the synthesis of ketones and ketoacids of the pyrrole, selenophene, and thiophene series. Tetraacyloxysilanes and acyloxytrichlorosilanes were used as acylating agents, in the presence of different metal chlorides. Triacyloxyboranes and tetracetoxygermane were found useful for the allylation of benzene and thiophene.

In a series of saturated heterocyclic compounds with two heteroatoms Yur'ev found a useful method for the synthesis of N-(β-mercaptoethyl) arylamines and hence 3-arylthiazolidines, as well as their derivatives with functional groups in position 2.

In latter years, Yur'ev intensively studied the chemistry of selenophene, the little studied isologue of furan and thiophene. He developed a catalytic method of synthesizing selenophene and homologues by the interaction of hydrocarbons, with not less than four atoms of carbon, and selenium in the presence of chromic and aluminum oxides at 450-500°. He also studied in detail metallation, aminometallation, chlorometallation, nitration, thionation, halogenation, and acylation of selenophene, its homologues and derivatives. From 2-acetoselenophene he prepared β-diketones of the selenophene series and studied their properties in detail.

As a result of these many investigations, the place of selenophene in the series of heteroaromatic systems was established. He showed that, in those reactions in which the heterocycles show electron-donor properties, selenophene occupies a position between furan and thiophene. With respect to electron-acceptor properties, selenophene also lies between thiophene and benzene. He also established the possibility of the practical application of derivatives of the thiophene series.

In 1961, for his work on heterocyclic compounds, Yur'ev was presented with the Zelinskii Award by the Praesidium of the Academy of Sciences USSR.

Even this brief account of Yur'ev's career must reveal the many facets of his scientific interests, his wide and penetrating creative projects. However, his contribution to the chemistry of heterocyclic compounds is inestimable and his name is inseparably linked with this field of organic chemistry.

Yur'ev's academic record was brilliant. He was a talented teacher and lecturer, distinguished experimentalist and savant of synthetic organic chemistry. In 1938 he prepared a new and original course entitled: "Synthetic Methods of Organic Chemistry." This program is still followed by chemistry students in Moscow and other Russian universities. Yur'ev's lectures were always extremely interesting and clearly presented. Skilfully, he selected his reactions from the vast material available and explained them to his audience in a logical, clear, and exciting manner.

In 1938, under Yur'ev's leadership, a program to prepare a comprehensive manual of organic chemistry was organized. This has become a model for subsequent courses in all the chemical faculties of Russian universities.

Yur'ev is the author of a comprehensive text on "Practical Work in Organic Chemistry," for university chemical faculties, which has now reached its third edition. This text has an original approach and contains detailed descriptions of the various methods of synthesizing examples of each class of substance. In the short period (1957-1965) the text was reissued three times and undoubtedly will appear again, but now his untimely death has ended Yur'ev's contribution to these future editions.

Yur'ev was an excellent educator. Exacting and strict, but at the same time unusually sincere and attentive, he was very fond of students and strove to develop all their better traits. He instilled in his students an active relationship to life, a desire for high principles, industry, and accuracy in their work. A fervent patriot, the aims of the Soviet State were also his aims.

Yur'ev trained hundreds of qualified chemists, many now distinguished heads of large scientific and industrial laboratories. Under his immediate direction, over 150 work diplomas and 32 master's diplomas were awarded and numerous doctoral theses were presented.

Yur'ev was a capable organizer. He played a leading role in the development of the Chemical Faculty at Moscow State University, and especially the Department of Organic Chemistry. He enthusiastically planned new university buildings.

In 1955, Yur'ev sat on the All-Union Scientific Commission for the Utilization of Pentose-Containing Materials. From 1947, he was a member of the Editorial Board of the Journal of General Chemistry, and from 1965 of Chemistry of Heterocyclic Compounds. Yur'ev performed these duties with energy and zest. He was an unusually careful and considerate editor, exacting not only with others but also with himself. A series of monographs, including the well-known multi-volume publication Heterocyclic Substances, was edited by him.

Yur'ev was awarded the Order of the Red Banner of Labor and medals for his work.

Warm memories of Yur'ev, leading scholar, talented teacher, ardent patriot, and good-hearted man, will always be retained by those scientists, working comrades, and all Russian chemists who knew him.

His editorial colleagues on this Journal deeply mourn their tragic loss and express sincere condolence to his widow, Professor Rosa Yakovlevna Levinaya, Doctor of Chemical Sciences.