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The chemistry of carbenes

Carbenes, which are labile compounds of divalent carbon, constitute, together with carbonium ions, carbanions, and free radicals, one of the main classes of intermediates in organic reactions, which determine their mechanisms and the nature of the final products.

As an independent field, the chemistry of carbenes and their analogues has been developing vigorously for about 30 years and the advances have been described in numerous monographs, collected volumes, and reviews. Numerous scientific conferences, symposia, and individual reports have been devoted to the examination of various aspects of this field. In particular, All-Union Conferences on the Chemistry of Carbenes have been held regularly in our country since 1972.

At the same time, the review and monograph literature on the chemistry of carbenes available to the Soviet reader is clearly inadequate and is inconsistent with the importance of this field and with the contribution which Soviet chemists have made to it. Thus Kirmse's monograph, the only one translated into Russian, was published in 1966 (translation of the original 1964 edition) and the specialist issue of the Journal of the All-Union Mendeleev Chemical Society (1979, Vol. XXIV, No. 5), devoted to the consideration of various aspects of the chemistry of carbenes and their analogues, was published 10 years ago.

The present topical issue of the journal *Uspekhi Khimii* (Russian Chemical Reviews) is devoted to the latest advances in the chemistry of carbenes and their complexes and includes reviews prepared on the basis of plenary reports presented at the IV All-Union Conference on the Chemistry of Carbenes (Moscow, September, 1987).

The issue begins with the review by V I Minkin, B Ya Simkin, and M N Glukhovtsev, which surveys the numerous results of quantum-chemical calculations of the electronic and geometrical structures of carbenes. The data presented by the authors convincingly demonstrate the high reliability of current computational methods as regards the quantitative estimation of almost all the features of the structure and reactivity of these species.

On the other hand, the review by P S Zuev and O M Nefedov deals with the latest advances achieved by one of the most informative experimental methods for the direct investigation of the spectra and structures of carbenes and other unstable molecules—namely the method of low-temperature matrix spectroscopy. In recent years, this method has been used not only for the stabilisation and spectroscopic identification of carbenes but also for the direct observation of their reactions occurring in low-temperature matrices.

The review by V A Petrosyan and M E Niyazymbetov is devoted to the consideration of one of the comparatively new but extremely promising aspects of the chemistry of carbenes and their analogues—their electrochemical generation and the creation of highly selective processes for electrochemical carbene synthesis.

The review by R R Kostikov and A P Molchanov presents the latest results on the chemistry of halogen-containing carbenes—one of the classes of these intermediates most thoroughly investigated and widely used in organic synthesis. The review includes both theoretical and experimental data on the structure and reactivity of these species as well as information about new methods for their generation.

Another important class of carbenes widely used in synthesis comprises alkoxycarbonylcarbenes, which can be easily generated from readily available alkyl diazoacetates. Certain aspects of the chemistry of alkoxycarbonylcarbenes and the cyclopropene-3-carboxylic acid esters related to them, as promising intermediates in organic synthesis (synthons), have been surveyed by M N Protopopova and E A Shapiro.

Finally, the last two reviews refer to the chemistry of carbene complexes of transition metals. Perhaps the most extensive and impressive results, including those of great practical value, have been obtained in this field in recent years. In particular, the review by I I Moiseeva deals with the role of carbene complexes—reliably identified or postulated in various catalytic processes including those of decisive importance for many fields of organic and petrochemical synthesis. On the other hand, the review by A P Antonova and A A Ioganson is devoted to the consideration of coordination compounds of unsaturated carbenes. It is precisely by virtue of coordination that these carbenes have been used effectively in the synthesis of many important organic and organometallic compounds and many of the reactions involving these complexes can be regarded as model processes and the complexes themselves are unique objects for structural studies.

A series of reviews devoted to the use of carbenes in specific organic synthesis and also the chemistry of nitrenes (the nitrogen analogues of carbenes) will be published in the next issue of the journal *Uspekhi Khimii*.

It is to be hoped that the publication of reviews on the present state of the chemistry of carbenes and their analogues will prove useful to a wide range of readers, will stimulate interest in this field, and will promote its further development in our country.

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