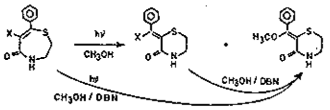
Under normal irradiation conditions a dimerisation of the reactants could be observed with the aid of MS (- via ene-reaction and/ or 2+2-cycloaddition ?). Monitoring this reaction while irradiating in an NMR-tube, from the NMR-signals a disrotatoric intramolecular cyclisation can be concluded. But the bicyclic photoproduct has only a short lifetime being converted again to the 7-membered starting material on standing at 45 °C in 10 minutes.

In the presence of Triplet-benzophenone a **Norrish-Type** II-cleavage of the lactimether group occurs.

Upon irradiation of the chlorinated 1,4-thiazepinones a new 1,4-thiazepine-1,4-thiazine-ring contraction is found:



The mechanism of this surprising transformation reaction could not yet be cleared and is at present under investigation.

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PL 12

THE ROLE OF NITRENES IN THE REACTIONS OF THE FORMATION OF SOME NITROGEN HETEROCYCLES

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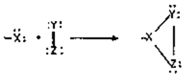
The mechanism of the formation of ring structures is doubtless one of the main problems in modern chemistry of heterocyclic compounds. Among many possible reactions leading to the closure of certain fragments of the backbone of the molecule into ring structures, increasing attention has been directed in recent years to the reactions in which ring formation is carried out by very active uncharged intermediate particles containing atoms with incomplete (sextet) electron shells (carbenes $R_2C:$, nitrenes $RN:$ and some other similar particles)

The interest for the reactive sextet intermediates in the chemistry of heterocyclic compounds has been aroused fairly recently and stimulated by the progress in the chemistry of carbenes. The literature on this subject is numerous and is rapidly increasing as is shown in special reviews on the synthesis of heterocycles via carbenes[1]) and nitrenes[2,3]). In this paper we will confine ourselves to one aspect of the problem: the proof of the nitrene mechanism of the formation of heterocycles. One of the simplest examples of this mechanism is considered here in detail. This problem is relatively urgent since there is a rapidly growing stream of original papers in which we can find discussions concerning the actual part played by the sextet intermediates; in many cases even their existence is considered doubtfull. On the other hand, there are many new interesting and important papers on the synthesis of heterocyclic compounds in which the participation of nitrenes is assumed to be the most probable or selfevident mechanism of ring formation without any particular confirmations.

If we try to classify the possible routes to ring formation via sextet intermediate particles it is possible to establish two general types of reactions.

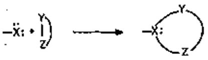
1. Addition to multiple bonds



and

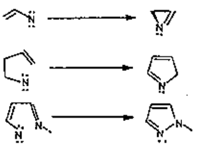
(in this case any reacting fragments can contain heteroatoms)

2. Insertion of "sextet" atoms into single bonds of a ring present in the reagent with its broadening or their insertion into other bonds of the same particle with ring formation as a result of the isomerization of the most reactive intermediate particle



and

For some unsaturated nitrenes valency isomerization with the formation of a heterocycle is also of great importance (transformation of vinylnitrene, butadienylnitrenes and azabutadienylnitrenes into azirine, pyrrols and pyrazols, respectively, and similar transformations of arylnitrenes):



Some "sextet" particles can exhibit distinct characteristics of 1,3-dipoles(ketocarbenes such as $O{=}\underset{|}{C}{-}\underset{|}{C}:\ \longleftrightarrow\ \overset{-}{O}{-}\underset{|}{C}{=}\underset{|}{\overset{+}{C}}$) and in this case they can interact with multiple bonds according to the scheme of 1,3-dipole addition with the formation of various five — membered heterocycles. However, the same heterocycles can also appear as a result of the rearrangements of primary products of 1,1-cycloaddition containing three-membered rings readily undergoing isomerization (works of Prof. I. A. Diakonov and co-workers at Leningrad University on the Mechanism of the formation of furans in the reactions of acylcarbenes with acetylenic hydrocarbons).

The tendency of "sextet" particles toward the cycloaddition reactions and insertion is determined by their fine electronic structure (the actual distribution of electron density) and even particles with identical "sextet" atoms can exhibit quite different abilities for forming heterocycles. It cannot either be ruled out that rings can close simultaneously via excluding the intermediate formation of nitrenes. The contribution of each of these mechanisms can vary depending on the conditions of the process. At present the number of the types of heterocycles in the formation of which the participation of nitrenes is considered to be possible is very great (about 30)[3] and the total number of such reactions (taking into account the possibility of using different methods of the generation of nitrenes from different precursors is several times greater. It should be added that heterocycles synthesized by these methods include some very important and interesting natural compounds and their analogues[2].

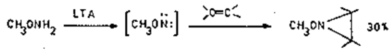
Hence, the mechanisms of this extensive group of syntheses of heterocyclic compounds deserve further detailed studies. The problem of proving the participation of nitrenes in these processes becomes particularly interesting. The isolation of reactive intermediate particles with a direct determination of their structure by a physical method should be the most confincing proof of this participation. However, nitrene intermediates are so short-lived that so far no information is available on their isolation. The following three indirect proofs of the existence of these unstable intermediates should be noted particularly:

1. Predictions (and carrying out) of some unknown reactions proceeding from the possible formation of nitrenes and the assumptions or theoretical (quantum-chemical) data concerning their structure and, hence, their properties and reactivities.
2. Investigations of the stereochemical aspects of this reaction and the conclusions on its mechanism obtained from them.
3. The establishment of genetic relationships between several products of this reaction and the proof of the possibility of their formation from the same intermediate.

The possibility of the formation of alkoxyaziridines by adding hypothetical oxynitrenes to double carbon-carbon bond is examined as a typical example illustrating the state of the problem of the nitrene mechanism of the formation of heterocycles and the character of possible arguments in this field:

N-Alkoxyaziridines were unknown before 1970 and alkoxynitrenes were mentioned for the first time ten years ago by Boyer and Woodyard.[4]

In 1970 Brois[5] studying a very interesting problem of the stereoisomerism of trivalent nitrogen compounds came to the conclusion that high pyramidal stability of nitrogen and the existence of stereoisomers with different steric position of alkoxy groups should be expected for N-alkoxyaziridines. Proceeding from a possible analogy with the synthesis of cyclopropanes via carbenes and supposing that methoxynitrene can be obtained the oxidation of methoxyamine by lead tetracetate and, finally, assuming that methoxynitrene is electrophilic like the simplest carbenes, Brois synthesized methoxytetramethylaziridine according to the scheme:



Quantum-mechanical calculations of fine electronic structure of the simplest oxynitrenes[6] confirmed the irresemblance to electrophilic carbenes (and at the same time showed great differences in the charge distribution between them and aminonitrenes). This conclusion was confirmed when a whole series of alkoxyaziridines was synthesized. Their yields differed in accordance with the expected values for olefines with various degrees of substitution[7]. Experiments with methoxyamine and stereoisomeric butenes-2 showed that the reaction is strictly stereospecific: cis-butene-2 yielded only cis-2,3-dimethyl-1-methoxy-aziridine (a mixture of syn-and anti-forms) and trans-butene-2 gave only trans-2,3-dimethyl-1-methoxyaziridine This result was interpreted as an argument supporting the existence of singlet oxynitrenes, primary products of alkoxyamine oxidation lead tetraacetate (LTA). However, in a paper appearing almost simultaneously[8] the authors have rejected the nitrene mechanism of the formation of alkoxyaziridines from alkoxyamines and olefines on the basis of their data that the reaction is not stereospecific in the case of N-butoxyamine. The stereochemical direction of this reaction is of fundamental importance for establishing its mechanism. Therefore the experiments with butoxyamine and butenes were repeated under identical conditions with a detailed chromato-mass spectrometric analysis of reaction mixtures. It was found[9] that in the work reported in ref.[8] a structural isomer of 2,3-dimethyl-1-butoxyaziridine 0-butylbutyral dioxime, was erroneously taken for it. Hence, the assertion that the formation of aziridines from butoxyamine is not stereospecific is unfounded.

O-alkyl ethers of oximes are always formed when alkoxyamines undergo oxidation by LTA and can be considered as the products of the rearrangement of intermediate alkoxynitrenes into oximes and of the interaction of the latter with the initial alkoxyamines:[10]

$$\left[RR'CHO\ddot{N}:\right]\xrightarrow{1,2\sim PR'CH} PR'CH{-}N{=}O \xrightarrow{1,3\sim H} RR'C{=}N{-}OH$$

$$RR'C{=}N{-}OH + RR'CHONH_2 \rightarrow RR'C{=}N{-}OCHRR' + H_2NOH$$

Rearrangement of alkoxynitrenes into nitroso-compounds and oximes is quite similar to the so called diazene-hydrazone rearrangement of their nitrogen analogues, aminonitrenes. Tertiary nitroso-compounds unable to isomerize into oximes can be isolated as final products of the oxidation of alkoxyamines with tertiary radicals[11]. All these data are in good agreement with the hypothesis on the generation of alkoxynitrenes via the oxidation of alkoxyamines and with the nitrene mechanism of the formation of aziridine rings.

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