PL 11

PHOTOCHEMISTRY—A MODERN TOOL IN HETEROCYCLIC CHEMISTRY—SOME SELECTED EXAMPLES

Heinrich Wohlff
Institut für Organische Chemie und Biochemie der Universität Bonn, Gerhard-Domagk-Straße 1, D-5300 Bonn — 1 Bundesrepublik Deutschland

In the first part heterocyclic molecules are compared with aliphatic, alicyclic and carbocyclic compounds regarding their reactivity in the excited state. In many cases a similarity and parallel behaviour can be stated, due to the fact that frequently excitation occurs selectively to carbonyl groups or aliphatic groups of the appropriate heterocyclic ring system.

Then new $\text{W} + \text{W} = \text{C}$ — cycloaddition reactions are presented of dihydroimidazoles to aromatic compounds (1), aminonitriles and heterocycles (2).

The stereochemistry of the photadducts, product distribution, side and secondary reactions are discussed in detail. Irradiation of dibromoethylenes in benzene results in a new example of an isolable 2$\text{+}$2-adduct to the benzene molecule:

Besides there is observed also double alkylation reaction and subsequent stilbene-analog photocyclization to give phenanthrene(9, 10$\text{c}$) = pyrene. DDMR upon irradiation add also smarable to uracil (2), while $\text{d}$-aminocrotonates add DDMR at the electron-rich $\text{C}$. Additionally new photoadducts of 2,5-dimethyl-1,3,4-oxadiazoles to uracils have been found (3).

The next part deals with photochemical and thermal reactions of 4-substituted 1,2,4-triazole-3,5-diones ($4$-$\text{R}$-$\text{TAD}$) (4, 5). Irradiation leads to fragmentation into CO, N$_2$ and isocyanates, while thermolysis gives — via a new radical intermediate: 4-phenyl-urazol — the Stollée($\text{d}$) s-triazole(1,2-$\text{a}$)-1,3-triazole:

Several other new and versatile addition-, cycloaddition- and decomposition reactions of the R-TAD are described.

The last part is devoted to a new approach towards the problem: electrolysis photoisomerization of 1,4-thiazepines into bicyclic molecules of the porphyrinoid (7). An improved synthesis of 1,4-thiazepines is presented as well as transformation reactions of these into suitable model compounds for carrying out photoinduced internal electrolytic reactions.
Under normal irradiation conditions a dimetalation of the reagents could be observed with the aid of MS (via one-reaction and/or 2+2-cyclodaddition). Monitoring this reaction while irradiating in an NMR-tube, from the NMR-signals a disrotatory intermolecular cyclisation can be concluded. But the bicyclic photoprodct 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 lactamtrier group occurs. Upon irradiation of the chlorinated 1,4-thiazepines a new 1,4-thiazepine-1,3-thiazine-ring contraction is found:

\[ \begin{align*}
&\text{CH}_{2}CN \quad \text{H} \quad \text{CH}_{2}CN \\
&\text{CH}_{2}CN \quad \text{H} \quad \text{CH}_{2}CN
\end{align*} \]

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

LITERATURE:


ACKNOWLEDGEMENT

Support of our work by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the BAYER AG is gratefully acknowledged.

PL 12

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

B. V. Ioffe

Leningrad University, USSR

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 RC\(^+\), nitrenes RN\(^-\), and some other similar particles)

The interest for the reactive sextet intermediates in the chemistry of heterocyclic compounds has been aroused recently and stimulated by the progress in the chemistry of carbenes. The literature on this subject is numerous and rapidly increasing as is shown in special reviews on the synthesis of heterocyclic compounds (1, 2) and nitrenes (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 doubtful. 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

\[ \begin{align*}
&\text{X}_1 \quad \text{Y}_1 \quad \text{Z}_1 \\
&\text{X}_2 \quad \text{Y}_2 \quad \text{Z}_2
\end{align*} \]

and

\[ \begin{align*}
&\text{X}_1 \quad \text{Y}_1 \quad \text{Z}_1 \\
&\text{X}_2 \quad \text{Y}_2 \quad \text{Z}_2
\end{align*} \]

(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

\[ \begin{align*}
&\text{X}_1 \quad \text{Y}_1 \quad \text{Z}_1 \\
&\text{X}_2 \quad \text{Y}_2 \quad \text{Z}_2
\end{align*} \]

and

\[ \begin{align*}
&\text{X}_1 \quad \text{Y}_1 \quad \text{Z}_1 \\
&\text{X}_2 \quad \text{Y}_2 \quad \text{Z}_2
\end{align*} \]

For some unsaturated nitrenes valency isomerization with the formation of a heterocycle is also of great importance (transformation of vinylnitrenes, butadienynitrenes and azabutadienynitrenes into azirines, pyrrols and pyrrolines, respectively, and similar transformations of arylnitrenes).