(7) transition from saturated to ethylenic, and further to acetylenic compounds resulted in the reduction of the basic strength by 0.7—0.8 and 2.0—2.2 pK units, respectively, the values consistent with the alteration of the electron-accepting capacity of the substituents;

(8) substitution of hydrogen for trimethylsilyl group in the 1-propargyl derivatives caused a slight increase in the basic strength of the compounds, which was, nevertheless, lower than that of the t-butyl compounds, due to the strong $(p-d)_\pi$ interaction between π electrons of the triple bond with free 3d-orbitals on the silicon atom in the organosilicon acetylenic amines;

(9) trimethylsilylmethyl- and neopentyl derivatives (α-amines) were less basic as compared to β-compounds.

The latter findings were contrasted by the linear correlation between pK_a and the inductive effect of the substituents. Persistent linear relationship between the basic strength of the 1-substituted heterylamines and σ^* was not obtained unless α-amines possessing abnormally low basic strength were excluded from the correlation analysis.

Decrease in the basic strength of organic amines is due to the steric shielding during solvatation of the basicity centre by the neopentyl group (which is also apparent on the molecular models), in the case of organosilicon compounds the reason lies in the intramolecular electronic interaction between the silicon and nitrogen atoms.

Inductive constants calculated for the trimethylsilylmethyl group (—0.17; —0.18; 0.176) on the basis of correlation equations are independent of the steric effect of heterocycles (E_S equals 0.51, 0.79, and 1.1, respectively) and are suggestive that the decrease in the electron-donating properties of the group is electronic in nature.

To investigate the effect of association on the chemical shift of chloroform in NMR spectra, we used dilution with 1-(trimethylsilylalkyl)pyrrolidines. The chemical shift (δ_K) was found to be proportional to the hydrogen bond stability, which was determined in the present case by the basic properties of the nitrogen atom.

Our data showed that electron-donating capacity of the nitrogen atom in α-amine (δ_K = —1.06) was lower not only with respect to β-amine (δ_K = —2.11) but also with respect to 1-propylpyrrolidine (δ_K = —1.54).

Similar results were obtained from ^{13}C and ^{29}Si NMR spectra for organosilicon derivatives of pyrrolidine and from determination of electron-donating capacity of nitrogen in pyrrolidine, piperidine and perhydroazepine derivatives by IR spectroscopy (as evidenced by $\Delta\upsilon C-D\ldots N$ shift of deuterochloroform).

Thus, by the use of various physico-chemical methods it was shown that besides + I-effect of the trialkylsilyl group in organosilicon α-amines exists another electronic effect acting in the opposite direction which is responsible for the decrease in the electron density on the nitrogen atom.

I am very graeful to R. Y. Sturkovich, E. Liepinš, T. V. Kashik, E. S. Deriglazova, E. I. Kositsyna, and M. Mägi who were engaged in the experiments, and to prof. M. G. Voronkov for the useful discussion.

PL 11

PHOTOCHEMISTRY A MODERN TOOL IN HETEROCYCLIC CHEMISTRY — SOME SELECTED EXAMPLES

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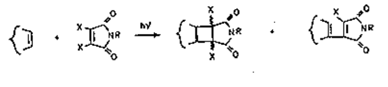
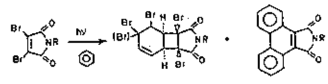
In the first part heterocyclic molecules are compared with aliphatic, olefinic and carbocyclic compounds regarding their reactivity in the excited state. In many cases a similar and parallel behaviour can be stated, due to the fact that frequently excitation occurs selectively to carbonyl groups or olefinic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

Then new $\pi 2s + \pi 2s$ — cycloaddition reactions are presented of dihalomaleimides to aromatic compounds (1), enaminoesters and heterocycles (2).

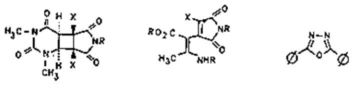


The stereochemistry of the photoadducts, product distribution, side and secondary reactions are discussed in detail. Irradiation of dibromomaleimide in benzene results in a new example of an isolable 2+2-adduct to the benzene molecule:

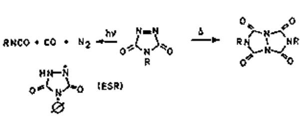


Besides there is observed also double alkylation reaction and subsequent stilbene-analog photocyclisation to give phenanthra[9, 10-c] = pyrroles. DXMI upon irradiation add also smothly to uracil (2), whille β-aminocrotonates add DXMI at the electron-rich C_β.

Additionally new photoreactions of 2,5-diaryl-1,3,4-oxadiazoles to uracils have been found (3).

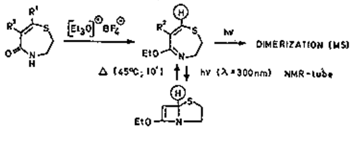


The next part deals with photochemical and thermal reactions of 4-substituted 1,2,4-Triazolin-3,5-diones („4-R-TAD") (4,5). Irradiation leads to fragmentation into CO, N_2 and Isocyanates, while thermolysis gives — via a new radical intermediate: 4-phenyl-urazolyl — the Stollé-(6) s-triazolo[1,2-a]s-triazole:



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

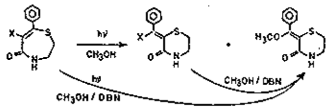
The last part is devoted to a new approach towards the problem: electrocyclic photoisomerization of 1,4-thiazepines into bicyclic molecules of the penam structure (7). An improved synthesis of 1,4-thiazepinones is presented as well as transformation reactions of these into suitable model compounds for carrying out photoinduced internal electrocyclic reactions.



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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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

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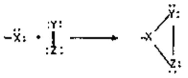
The mechanism of the formation of ring structures is doubtless one of the main problems in the modern chemistry of heterocyclic compounds. Among many possible reactions leading to the closure of certain fragments of the backbone of the molecule into ring structures, increasing attention has been directed 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):