

THE INFLUENCE OF THE STRUCTURE OF OXYGEN AND NITROGEN CONTAINING HETEROCYCLES ON THEIR CHROMATOGRAPHIC BEHAVIOUR

A. A. Anderson, M. V. Shimanska

Institute of Organic Synthesis, Academy of Sciences of the Latvian SSR, Riga, USSR

Gas-chromatographic behaviour of 5- and 6-membered nitrogen and oxygen containing heterocyclic compounds was studied with respect to their molecular structure. The value of retention indices I , homophy factors H and their differences ΔI and ΔH between nonpolar (apiezon M) and polar (polyethylene-glycol 2000) stationary phases were determined for the following series of compounds: pyrrole, pyrrolidine, pyridine, piperidine, pyrazine, piperazine, triethylenediamine, morpholine, furan, furanidine, tetrahydropyran, and dioxane. Retention indices I of the above series of compounds were found to be correlated with their boiling point and could be depicted by the linear equation $I = a(\text{boil. } t^\circ + b)$, where a and b are constant. On the diagrams representing the values of retention indices on sorbent of various polarity, heterocyclic compounds belonging to different series, were characterized by straight lines situated in various parts of the plot, according to their affinity to specific intermolecular interaction with the stationary phases. Such interaction was best pronounced in N-unsubstituted pyrroles, followed by pyrazines and pyridines; where- as N-substituted saturated heterocyclic compounds, furan, furanidine and their derivatives interact with the sorbent in smaller extent.

The values of I , H , ΔI , and ΔH in heterocyclic systems were shown to consist of individual contributions of all structural elements, that constitute the molecule. The contributions to the values of I , H , ΔI , and ΔH of such structural elements as heteroatoms O and N, methyl and amino groups with respect to their position in the ring were measured. Thus, substitution of methylene group for an oxygen atom in the ring of cyclopentadiene at 180°C is characterized by the value of 75 units, while in the ring of cyclopentane, cyclohexane and piperidine, by 180 units. The corresponding values for $\text{CH}_2 \rightarrow \text{NH}$ substitution in the cyclopentanes, cyclohexane, piperidine, tetrahydropyran, and pentadiene rings are 255, 220, 220, 210, and 360 units, respectively. Substitution of CH_2 for N in the aromatic nucleus gives the following values of ΔH increments, 195, 175, 200, 200, 170, 90, 55 in the cases of benzene, o-, m-, and p-positions in toluene, o-position in m-xylene, and m- and p-positions in pyridine, respectively.

The values of the increments measured were found to differ significantly from those obtained for the same structural elements in aliphatic and aromatic compounds. The effect of steric hindrance on the values of N atom increments in I , H , ΔI , and ΔH was noted. On the basis of the additivity of increments contributed by different structural elements a method for qualitative analysis of oxygen and nitrogen containing heterocyclic compounds without the use of standard substances has been proposed.

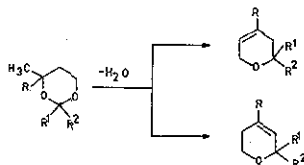
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PREPARATION AND SOME HETEROLYTIC REACTIONS OF CYCLIC ACETALS

E. A. Kantor

Ufa Petroleum Institute, Ufa, USSR

Preparation of cyclic acetals and their heteroanalogues as a result of acetalization reaction, reacetalization and exchange of aldehyde, ketones, glycols, α - and β -oxides, orthoesters, 1,3-dioxas, oxathias and dithiacycloalkanes was investigated. It was stated that some 1,3-dioxanes intermolecularly dehydrated into isomeric dihydropyranes under acid catalysis conditions:

R, R¹, R² = alkyl, cycloalkyl, phenyl.

The possibility of recyclization is provided by the presence of electrodonor substituents at C₄.

Alkyl, phenoxy- and amino-derivatives were prepared by the reaction of substitution of halogen- and alkoxy-containing 1,3-dioxacyclanes.

By NMR ¹H and ¹³C methods configuration and conformation of synthesized substances are designed.

By kinetic methods some rules of discussed reactions are stated and they are coordinated with quantum-chemical calculations.

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SYNTHESIS AND STRUCTURE OF 1,3-OXAZOLIDENES

U. B. Imshev, A. U. Stepanyants

Ufa Petroleum Institute, Ufa, USSR

3-alkyl(aryl)-1,3-oxazolidenes were synthesized by condensation of oxyethylalkyl (aryl) amines with carbonyl-containing compounds. Structure and stereochemistry of heterocyclic compounds obtained were studied by NMR on the nuclei of ¹H and ¹³C. It was shown that formaldehyde derivatives are subjected to quick pseudorotation resulting in protons of methylene groups adjacent with a heteroatom appearing as two triplets. Complex multiplet from 4 protons in PMR-spectrum of 2 alkyl (aryl)-1,3-oxazolidenes is observed. It shows non-equivalence of all protons at C⁴ and C⁵ carbon atoms. The influence of electro-donor and acceptor substituents in the second position of ring on values of chemical shifts of nuclei ¹³C in 1,3-oxazolidene-cycle and alkyl (aryl) group was studied.

Activity of 1,3-oxazolidenes in heterocyclic reactions was determined and correlation between reactivity and parameters of NMR-spectrum was found.

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INVESTIGATIONS IN THE FIELD OF CHEMISTRY AND TECHNOLOGY OF 1,3-DIHETEROCYCLANES

D. L. Rakhmonkulov

Ufa Petroleum Institute, Ufa, USSR

Data concerning reaction mechanisms of 1,3-dioxacyclanes formation by condensation of aldehydes with olefins, acetalization and reacetalization are given.

Synthetic potentials of acid-catalyzed conversions of 1,3-dioxacyclanes under the action of alcohols, thiols, amines and esters are studied.

It has been shown that in the limiting stage the splitting of heterocycle along carbon-heteroatom bond takes place.

Phenoxy-, amino-, alkoxy-substituted 1,3-dioxacyclanes were investigated.

General rules of addition and substitution reactions in cyclic acetals are discussed. It has been stated that preparation of thermodynamically unstable stereoisomers in alkyl 1,3-dioxacyclanes series is possible when initiated by donors of free radicals addition of cyclic acetals to ethylene.