



1,2-HYDROGEN MIGRATION IN AMINOALKYL RADICALS IN AMINATION REACTIONS OF α -OLEPHINS

T. A. Aslanov,^[a] E. T. Aslanova,^{[a]*} N. R. Bektashi,^[a] A. H. Azizov^[a] and D. R. Nurullayeva^[a]

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The amination of α -olefins (C_4 - C_7) in the $NH_2OH \cdot HCl - TiCl_3$ oxidation-reduction system was investigated and a number of mono- and diamines were prepared. It has been found that in the attack of NH_2 -radical to olefin a hydrogen migration from first carbon to second one takes place. It has been shown that in the reaction products, besides the desired individual amines, telomers, the molecular masses of which are approximately within the ranges of $M_n = 460$ -800, were also detected.

* Corresponding Authors

Fax: (+99418) 642-04-00

E-Mail: ipoma@science.az

[a] Institute of Polymer Materials, Azerbaijan National Academy of Sciences, 124, S.Vurgun str., Az5004, Sumgait, Azerbaijan

Introduction

A study of the molecular rearrangements has a great value for establishment of mechanisms of the chemical reactions and realization of the directed organic synthesis. As it was known, the rearrangements are the reactions, in the course of which a substituent is displaced inside of the molecule from one place to another, breaking an old bond and creating a new.¹ There are 2 types of the rearrangements, rearrangements with reconstruction of carbon skeleton and rearrangements with conservation of carbon skeleton.

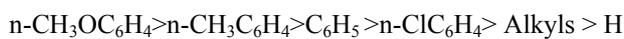
There are many rearrangements in the course of which a substituent from the carbon atom is transferred to the neighboring carbon, nitrogen or oxygen atoms. The similar 1,2-displacements can be caused by availability of electrons sextet (nucleophilic rearrangement), free electron pair of atom B (electrophilic rearrangement) or unpaired electron (radical rearrangement).

It has been reported earlier that in a number of the chemical reactions successive rearrangements take place.² Such reactions cause a lot of difficulties in establishment of the structure of the products.

It has been held earlier that, in solutions, the rearrangements of radicals are impossible or such processes are rare. So, Dewar³ has explained the impossibility of isomerization of fatty radicals stating that in this case the stable π -complexes cannot be formed. Moreover, the absence of the rearrangement in neopentyl residue in action of sodium on neopentyl chloride has been cited as a proof of radical mechanism of Wurtz reaction.⁴

The first homolytic rearrangement proceeding in liquid phase was reported by Kharash in 1944, rearrangement of neophilic (2-phenyl-2,2-dimethylethyl) radical to a tertiary radical. Freidlina with collaborators (1950-1965) have

systematically investigated the homolytic rearrangements of the aliphatic unsaturated haloid substituted compounds, rearrangements of allyl type.^{5,6} Nesmeyanov with collaborators⁵ have studied the isomerization of the radicals with 1,2-chlorine transfer. During study of pinacolone rearrangement occurring by the action of acids, particularly Lewis acids on pinacoles, Tiffen, Orekhov and Bakhman have studied in detail the ease of migration of radicals in this rearrangement.⁷ The order of ease of migration the radicals has been reported as the following series:



Reviews devoted to the rearrangements of radicals in the liquid phase are extremely rare. We could find only a small review published in Japan language,⁸ and a brief summary about some questions of the rearrangement of radicals in solutions.^{9,10}

This work is devoted to reactions of NH_2 -radicals with α -olefins. It was known that NH_2 -radicals take one of the central places in the chemistry of free radicals because they are the founder of an extensive series of nitrogen-centered radicals important for organic synthesis. At the same time, their reactions with organic compounds have not been investigated enough. There are few reports available in the literature that NH_2 -radicals can be added to 1,3-dienes. On the basis of this reaction the synthesis of unsaturated diamines has been carried out. The reaction of NH_2 -radicals with the simplest α -olefins has not been investigated until now, although it opens the most rational way of transition from unsaturated hydrocarbons to aliphatic amines.

In connection with above-mentioned one, the purpose of our work is the investigation of reaction of free-radical amination of α -olefins of composition C_4 - C_7 in the oxidation-reduction system of $NH_2OH \cdot HCl - TiCl_3$.

Experimental

The amination of α -olefins was carried out on basis of reported methodology.¹¹

The $^1\text{H-NMR}$ -spectra were taken on a T-80 Varian spectrometer with working frequency 80 MHz, solvent was CCl_4 with hexamethyldisiloxane (HMDSO) as an internal standard. The chemical shifts (δ ppm) were measured in a scale with exactness 0.01 ppm. The IR-spectra were taken on a Specord M-80 apparatus in the vaseline oil.

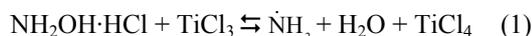
The chromatographic investigations were carried out by the methods of gas-liquid, exclusion and adsorption liquid chromatography (GLC, ELC and ALC). The analysis of amines by a method of GLC was carried out on a Khrom-31 apparatus, gas-bearer was helium, column temperature 130-140 $^\circ\text{C}$, column length 2.4 m, $d = 4$ mm, Chromaton + 1 % Carbowax served as a hard phase. The investigations by the methods of ELC and ALC were carried out on the high-effective liquid chromatograph of Czech firm, Kovo, with two columns by the size of 3.3×150 mm, filled with Separon SGX adsorbents, with diameter of pores 100 Å and Separon SGXC18 in the reversed phase respectively, particle size being 7 μm . There were chosen two-detector variants of these methods with use of UV-spectrophotometric ($\lambda = 254$ nm) and refractometric detectors. Eluents: dimethylformamide and methanol + water (75:25 rev. %). Their feed rate was 0.3 mL min^{-1} , temperature = 20-25 $^\circ\text{C}$.

The molecular weights (MW) of amination products have been established on calibration dependence between $\log M$ and V_R prepared in ALC regime with application of mono- and diamino-hexene and polyethylene glycol standards,¹² and also with use of the universal calibration dependence presented in an earlier work.¹³

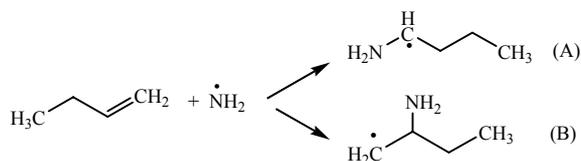
Results and Discussion

Structure of amination reaction products of 1-butene

For synthesis of amino compounds on the basis of free-radical amination of α -olefins, generation of amine radical by the oxidation-reduction system $\text{NH}_2\text{OH}\cdot\text{HCl}\text{-TiCl}_3$ has been used. According to the previous reports of this reaction,^{14,15} a formation of NH_2 is presented as:



For the generation of NH_2 radical, the oxidation-reduction system described earlier^{14,15} has been chosen with only difference that instead of TiCl_3 taken in equimolar amount to hydroxylamine, a much smaller amounts of TiCl_4 has been taken, which reduced in TiCl_3 by hydrogen, generated in situ with Zn/HCl . During amination of α -olefins, as a result of their reaction with NH_2 -radical, an aminoalkyl free radical is formed, the low selectivity of which leads to the formation of various products. An amination of 1-butene occurs on the following scheme



Scheme 1. Amination of 1-butene

Because of the high reactivity of radicals (A) and (B), a mixture of various amino compounds has resulted on the amination of 1-butene. During distillation of the reaction products two fractions with wide range of boiling temperature of 60-90 $^\circ\text{C}$ and 50-78 $^\circ\text{C}$ (5 mmHg) were obtained. The analysis of both fractions by a method of gas-liquid chromatography showed that the first of them is the mixture of monoamine of composition C_4 ,¹¹ and the second fraction is a mixture of primary and secondary diamines.

MW of the first fraction determined by cryoscopic method is 73.00, corresponding to a monoamine. From multiple experiments by precise purification of one fraction at boiling temperature 76-78 $^\circ\text{C}$ on column the isomer (98.8 %) corresponding to the second peak on chromatogram has been isolated. The calculated and found molecular rectification corresponded to butylamine ($MR_{D \text{ calc}} = 27.30$; $MR_{D \text{ found}} = 26.90$). The IR- and PMR-spectra of this substance were taken. In the IR-spectrum the characteristic absorption bands of aminogroup (valence vibrations) ν_{as} and ν_{s} at 3300 and 3370 cm^{-1} , deformation vibrations δ_{s} 840, 1400-1440 cm^{-1} , CH_2 -groups ν_{s} 2850 cm^{-1} , δ_{s} 1470 cm^{-1} , CH_3 -groups ν_{as} 2960 cm^{-1} , ν_{s} 2970 cm^{-1} have been observed. In the $^1\text{H-NMR}$ -spectrum, the characteristic chemical shifts in the field of $\delta=1.05$, 1.3, 1.75 and 3.5 ppm, corresponding to protons in the groups NH_2 , CH_3 , $\text{CH}_2\text{-C}$ and $\text{CH}_2\text{-N}$, with relation of the integral intensities 4:6:8:4, which confirms it to be butylamine.

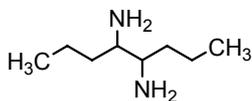
The IR- and $^1\text{H-NMR}$ spectra of monoamine fraction boiling between 60 and 90 $^\circ\text{C}$ indicated to presence of 2-aminobutane in considerable quantity in it, supported by a 18 % chromatographic peak of this compound. Consequently, an activation of 1-butene in the present reaction takes place mainly in position 2, and only a small amount of butylamine is formed as a result of the attack of olefin molecule by NH_2 -radical to position 1.

During chromatography of the fraction, boiling between 50 and 78 $^\circ\text{C}$ (5 mmHg.), after repeated precise rectification on two different sorbents, three peaks appeared in the chromatogram. The molecular refraction found and calculated for proposed structures of formed diamino compounds corresponded to $MR_{D \text{ calc.}} = 46.05$ and $MR_{D \text{ found.}} = 45.78$. In the IR-spectra of this fraction, the characteristic absorption bands of aminogroup ν_{s} , ν_{as} at 3370, 3300, 1640 cm^{-1} , CH_2 -group at ν_{as} - 2850 cm^{-1} , CH_3 -group at δ_{as} 2960, δ 1460 cm^{-1} , and for CH -group at δ 1340 cm^{-1} have been observed.

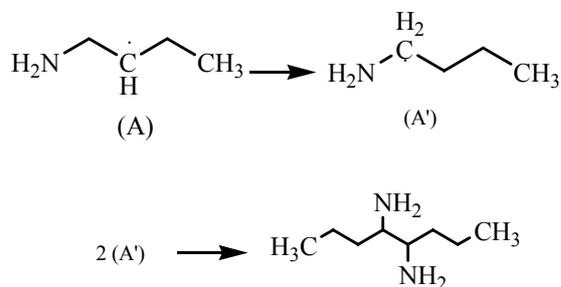
By precise rectification on vacuum column, the isomer corresponding to third peak on the chromatogram has been isolated. In the $^1\text{H-NMR}$ spectrum of this fraction, a number of groups of signals in the field of high areas were observed. In the range of 0.7-1.4 ppm there appeared two superimposed signals with unresolved multiplets. Besides, the signal with center at 0.85 ppm corresponded to the ten protons of fragment $-\text{CH}_2\text{-CH}_3$ on chemical shift and integral intensity, and other one with center at 1.2 ppm showed the superimposed signals of two methylene groups located in β -position to nitrogen atom. Four protons with $\delta = 1.63$ ppm corresponding to protons of two amine groups (NH_2)₂. On dilution, the signal from amine protons displaced to the field of strong areas ($\delta = 1.02$ ppm), which also witnessed an enhancement of sharpness of amino group signals. It may be noted that protons of amino groups participate in chemical exchange and therefore their

chemical shift unlike other signals is displaced with change of concentration. The signal at $\delta = 2.5$ ppm on integral intensity corresponded to two protons. This signal should be attributed to methine protons at the nitrogen, a chemical shift of which is well consistent with the literary data.¹⁶⁻¹⁹

The assignment of integral intensities of protons of groups CH : NH₂ : -CH₂-CH₂-CH₃ equal to 8 : 15 : 56, exactly corresponding to the structure of 4,5-diaminooctane.



As the attack of NH₂-radical on C₁ is predominating, the formation of 4,5-diaminooctane can be explained by assuming migration of a hydrogen from C₁ to C₂ and dimerization of the resultant aminoalkyl radical.



Scheme 2. Probable mechanism of the formation of 4,5-diaminooctane.

Structure of amination reaction products of 1-pentene

During amination of 1-pentene, the basic reaction products were mono-(C₅) and diamines (C₁₀) of isomeric composition. During vacuum distillation of the reaction product two fractions with boiling temperature, 95-106 °C and 90-100 °C (6 mmHg) have been isolated.

The chromatography of fraction boiling at temperature 95-106 °C indicated the presence of two peaks corresponding to two isomeric amines in it. MW fractions determined cryoscopically showed the satisfactory correspondence between their measured and theoretically calculated values (87.10). This fraction was subjected to the repeated precise fractionation as a result of a fraction boiling at 104 °C has been isolated. Chromatography of this fraction on the two different sorbents indicated that it is an individual substance. The observed *MR_D* of this substance is 25.80, and calculated for 1-aminopentene is 26.20. In the IR-spectrum of this compounds the characteristic absorption bands of amino group i.e. valence vibrations ν_{as} and $\nu_s = 3300$ and 3370 cm⁻¹, deformation vibrations $\nu_{as}, \nu_s = 840, 1400-1440$ cm⁻¹, of CH₂-group $\nu_s 2850$ cm⁻¹, $\delta_s 1470$ cm⁻¹ and of CH₃-group $\nu_{as} 2960$ cm⁻¹, $\nu_s 2970$ cm⁻¹ were observed. In the ¹H-NMR spectrum there were the characteristic chemical shifts at 1.05, 1.75, 3.5 ppm corresponding to protons in NH₂, CH₃, CH₂-C, CH₂-N groups with relation of the integral intensities of 2:2:9, which confirmed the formation of 1-aminopentene.

In the IR-spectrum of the fractions with boiling temperature = 90-100 °C (6 mmHg), the characteristic absorption bands of amino group, ν_s and $\nu_{as} = 3370$ and 3300 cm⁻¹, $\delta 1640$ cm⁻¹, of CH₂-group $\nu_{as} 2850$ cm⁻¹, of CH₃-group $\nu_{as} 2960$ and $\delta 1460$ cm⁻¹, and of CH-group $\delta 1340$ cm⁻¹ were observed.

In the ¹H-NMR spectrum, in the region of high fields in the range of 0.7-1.4 two partially superimposed signals with unresolved multiplets were observed. The signal with center at 0.85 ppm and integral intensity of ten protons of the fragment corresponded to -CH₂-, -CH₃-, and other one with center at 1.20 ppm are the superposed signals of protons of two methylene groups located in β -position to nitrogen atom. The signals of four protons with $\delta = 1.63$ ppm corresponded to the amines displaced to strong fields ($\delta = 1.02$ ppm), with also witnessed the sharpness assignment of the amino group. The moderate signal at $\delta = 2.5$ ppm with integral intensity corresponding to two methylene protons is in agreement with literary data. The assignment of the integral intensities of protons in groups CH₃ : NH₂ : -CH₂-CH₂-CH₃ = 8 : 15 : 70 (calculation = 2 : 4 : 18) confirms the formation of 5,6-diaminodecane.

The results of the experiment indicated that with an increase in the molecular weight of the olefin the relative amount of diamine formed, as a result of dimerization of the initially formed aminoalkyl radicals, is decreased.

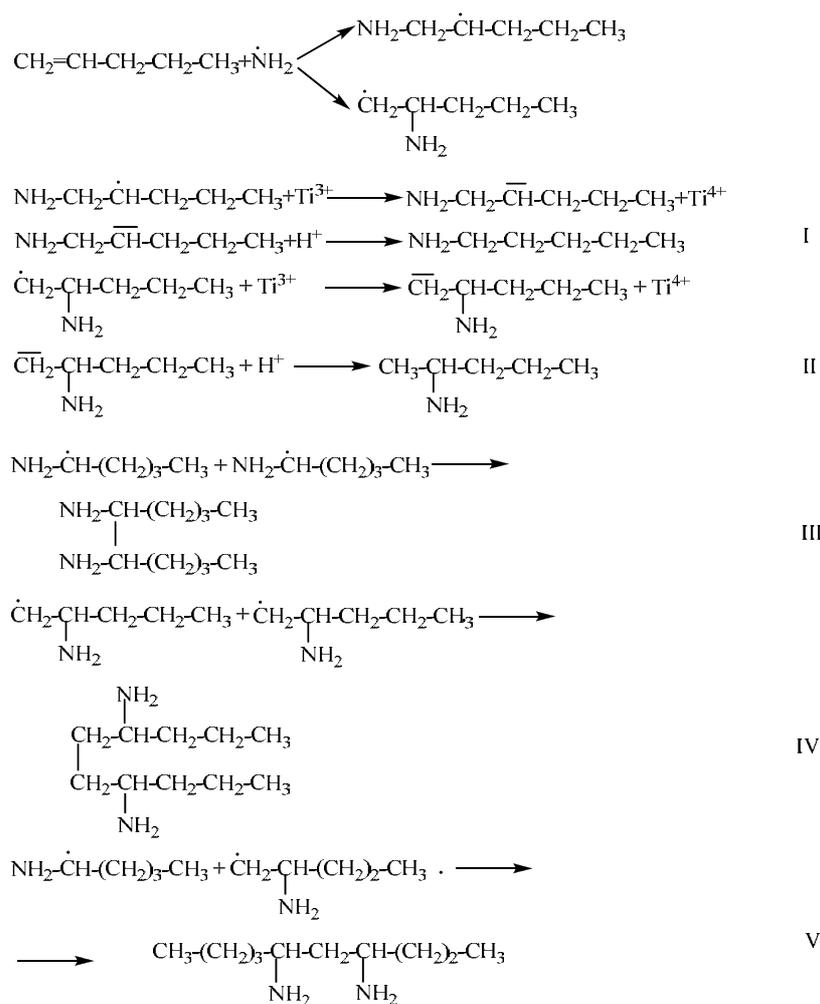
The results of establishment of structure of the amination reaction products of α -pentene by physicochemical methods of analysis showed that they are 1-aminopentane (I), 2-aminopentane (II), 5,6-diaminodecane (III), 4,7-diaminodecane (IV) and 4,6-diaminodecane (V). The formation of which has been presented in Scheme 3.

Structure of products of amination of 1-hexene

As a result of amination reaction of 1-hexene, two fractions with boiling temperature 132-133 °C and 120-130 °C (2 mmHg) have been isolated.

In the IR-spectrum of the first fraction the intensive absorption bands of valence vibrations of NH₂-group at 3386 and 3300 cm⁻¹, correspondingly to asymmetric (ν_{as}) and symmetric (ν_s) vibrations were observed. A calculation of ν_s on formula $\nu_s = 345.5 + 0.876 \cdot \nu_{as} = 345.5 + 0.876 \cdot 3386 = 3302$ cm⁻¹ is sufficiently well agreed with observing in 3300 cm⁻¹. The deformation vibrations of amino group were observed by the broadened bands in the range of 840 and 1600 cm⁻¹. The presence of CH₂-groups is confirmed by absorption bands in the range of 2920 cm⁻¹ and 1460 cm⁻¹.

In the NMR-spectrum of this fraction the characteristic singlet at $\delta = 0.95$ ppm, corresponding to two protons of NH₂-group was observed. The broadened (due to influence of nitrogen atom) signal at $\delta = 2.6$ ppm on integral intensity corresponded to two protons of CH₂-group. The chemical shift of these protons located at nitrogen atom is in accordance with the reported values. Triplet $\delta = 1$ ppm corresponded to methyl protons. The signals in the field of 1.15-1.25 ppm showed the presence of protons in methylene group connected to a carbon atom i.e. a -CH₂-C group.



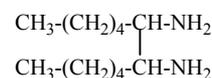
Scheme 3. Probable mechanism of the formation of products by the amination of 1-pentene.

Thus, in the spectrum there were the signals of the following groups: CH_3 : $-\text{CH}_2-\text{C} : \text{CH}_2-\text{N} : \text{NH}_2$ with ratio of integral intensities = 8:24:6:5, which are close to calculated quantity of protons in hexylamine, 3:8:2:2.

The investigation of fraction boiling at 120-130 °C (2 mmHg) by GLC showed the availability of two compounds in the ratio of 8:1. By precise fractionation of the fraction, a product present in the mixture in 87.6 % has been isolated. In the IR-spectrum of this product the absorption bands of amino group ($\nu_s, \nu_{as} = 3370$ and 3300 cm^{-1} , $\delta = 1640 \text{ cm}^{-1}$), CH_2 -group ($\nu_s = 2850 \text{ cm}^{-1}$), CH_3 -group ($\nu = 2960$, $\delta = 1460 \text{ cm}^{-1}$) and CH -group ($\delta = 1340 \text{ cm}^{-1}$) were observed. In the $^1\text{H-NMR}$ -spectrum of the same product there was a triplet with center at $\delta = 0.85$ ppm for 6 H corresponding to two methyl groups. The signal at $\delta = 1.2$ was assigned to the superimposed signals of methylene protons, methine groups and finally the signal at $\delta = 1.2$ met the superimposed signals of methylene protons located in β -position to nitrogen atom. Four protons at $\delta = 1.8$ corresponded to $(\text{NH}_2)_2$ amine protons. on dilution, the signal from amine protons was displaced to strong fields ($\delta = 1.25$ ppm), which supported their assignment to amino protons. The signal $\delta = 2.45$ corresponded to methine protons at nitrogen. Thus, in the spectrum there were

observed the signals of groups: CH_3 : $-\text{CH}_2-\text{C} : \text{CH}_2-\text{N} : \text{NH}_2$ with relation of integral intensities equal to 15:40:4:9, which is close to calculated quantity of protons (6:16:2:4) in molecule of diaminododecane.

Thus, on the basis of $^1\text{H-NMR}$ -spectrum the compound can be assigned the following formula.



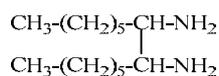
The investigations showed with an increase in molecular weight of the aminated α -olefin, the addition of NH_2 -radical to the second carbon atom is considerably decreased. As a result in addition to diamine, formed from dimerization of type (A) radical, high molecular weight telomeric products are also formed.

Structure of products of amination of 1-heptene

As a result of distillation of the amination products of heptene-1, two fractions have been isolated, with boiling at 158 °C and 135-140 °C (2 mmHg).

The chromatographic analysis showed the first fraction to be an individual compound. In the IR-spectrum of this compound, the characteristic absorption bands at 3295 cm^{-1} and 3380 cm^{-1} ($\nu_{\text{ss}}, \nu_{\text{as}}$), and also at 1600 and 840 cm^{-1} (deformation), corresponding to vibrations of amino group, at 2890 and 1340 cm^{-1} for CH_2 -groups and 2975 cm^{-1} for CH_3 - groups have been observed. In the $^1\text{H-NMR}$ -spectrum of this compound the signals corresponding to these groups are also observed. Triplet at $\delta = 0.95$ ppm corresponds to the protons of end methyl group and the superimposed signals of methylene groups, not connected with nitrogen atom, appear at $\delta = 1.3$ ppm. The signal at $\delta = 2.5\text{-}2.8$ ppm corresponds to the protons of $-\text{CH}_2\text{-N}$ and NH_2 -groups. The signals of NH_2 -groups appeared as a sharp singlet within the multiplet signals of $\text{CH}_2\text{-N}$. The integral intensity of the signals of $\text{CH}_3 : \text{CH}_2\text{-C} : \text{CH}_2\text{-N} : \text{NH}_2 = 17 : 50 : 20$ corresponding to the calculated quantity of protons in heptyl amine i.e. 3:10:4.

In the $^1\text{H-NMR}$ -spectrum of the fraction, boiling at $135\text{-}140\text{ }^\circ\text{C}$ (2 mmHg), the signals were analogous to those of 6,7- diaminododecane with only difference that the quantity of protons in hydrocarbon residue has increased. The ratio of integral intensities of the signals in the $^1\text{H-NMR}$ -spectrum of $\text{CH}_3 : \text{CH}_2 : \text{CH}_2 : \text{-N} : \text{NH}_2 = 21 : 68 : 16 : 8$ corresponded to the calculated value of $3 : 10 : 1 : 2$, which also confirmed the formation of 7,8-diaminotetradecane during amination of 1-heptene.



Mechanism of formation of telomers during amination of 1-hexene

The mechanism of the amination process of α -olefins and formation of high-molecular telomers therein has been investigated in the case 1-hexene. The analysis involved ALC on reversed phase and ELC with two-detector system of chromatography.²⁰ As a result of analyses of the reaction products by refractometric detection, 5 fractions have been detected, 3 of which correspond to the high-molecular telomers in a quantity of 5, 14 and 6 % with molecular weight $M_n = 794, 660$ and 478 , respectively. Two subsequent fractions consist of monoamine (70 %) and from mixture of isomers of diamino compounds, i.e. 6,7- and 5,8-diaminododecane (5 %). These compounds are the dimerization products of aminoalkyl radicals forming in attack of NH_2 -radical to molecule of 1-hexene, which leads to the proton transfer from first carbon atom to the second and vice versa from second to the first one. It has been established that the hydrogen migration also influences the isomeric structure of telomers products. So, unlike refractometer readings the signals of telomere fractions on the working wave (254 nm) of UV-detector have a multiplet character and consist of three maxima, which can be referred to various isomers of oligoaminohexene, most likely formed during proton migration between different carbon atoms.

Conclusions

1. It has been shown that the synthesis of amino compounds of $\text{C}_4\text{-C}_7$ α -olefins by the oxidation-reduction system $\text{NH}_2\text{OH}\cdot\text{HCl-TiCl}_3$ takes place by an attack of NH_2 -radical predominantly on first and to a lesser extent on second carbon atom, accompanied by hydrogen migration from C_1 to the C_2 (1,2-migration) and vice-versa (2,1-migration), leading to the formation of α - and β -monoaminoalkanes. A dimerization of arising aminoalkyl radicals leads to the formation of the higher diaminoalkanes.

2. It has been established that in the case of amination of 1-hexene and 1-heptene, along with the formation of individual aminoalkanes, telomerization of the corresponding olefins leading to appearance of fractions of oligomer amines with MW 500-800 (in the case of 1-hexene) and 700-950 (in the case of 1-heptene) takes place.

3. It has been established by a method of reversed-phase ALC in example hexene-1 that each telomer fraction consists of mixture of three isomers. So, on the working wave length of UV-spectroscopic detector ($\lambda = 254\text{ nm}$) the triplet signals corresponding to the different isomers of oligoaminohexene with the same MW have been fixed. It has been concluded in accordance with regularities of reversed-phase ALC that the separation of these isomers occurs in the order of decreasing of their polarity. The accordance of the first two isomers to more polar α - and β -oligoaminohexanes forming at 1,2- and 2,1-hydrogen migration and third, less polar isomer corresponding to oligohexane forming by hydrogen migration either from second to the third, or to the fourth carbon atom has been shown.

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