carborane) 3090, 3100 (η^5-C_5H_4). PMR spectrum (in C_6H_6, δ, ppm): 4.29 m, 3.97 m (η^5-C_5H_4), 3.29 s (CH carborane), 1.62 s ($Me_2S^{\oplus}$), 1.14 s (CH_3), 1.02 s (CH_3). The dimeric complex (VI) (0.1 g, 15%) of mp 203-204°C (with decomposition) and the dimeric dimethylsulfonium zwitterion (X) (0.27 g, 36%) brown crystals of mp 160-190°C (with decomposition, from C_6H_6–heptane) were also obtained. Found: C 41.02; H 7.28; S 3.94%. $C_{22}H_{47}B_{18}Fe_2S$. Calculated: C 40.70; H 7.27; S 4.93%. IR spectrum (ν, cm^{-1}): 2450-2650 (BH), 2880, 2940, 2970 (CH_3), 3050 (CH carborane), 3090, 3100, 3110 (η^5-C_5H_4). Complexes (IX), (VI), and (X) were separated with the aid of column chromatography as described above.

CONCLUSIONS

1. η^5-Isopropenylcyclopentadienyl-η^5-(3)-1,2-dicarbollyliron has been obtained containing the metal in both Fe(II) and Fe(III) forms.

2. The protonation of the double bond in η^5-isopropenylcyclopentadienyl-η^5-(3)-1,2-dicarbollyliron (II) with the formation of a tertiary carbocation has been investigated.

3. The carbocationic center was stabilized significantly less by the η^5-1,2-$C_2B_9\bar{H}_{11}$-3-Fe^{II}-η^5-C_5H_4- group than by the η^5-C_5H_5-3-Fe-η^5-1,2-$C_2B_9\bar{H}_{11}$-1- group.

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REACTION OF PHENYL DERIVATIVES OF LANTHANIDES WITH CARBONYL COMPOUNDS

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Not long ago, compounds of rare-earth elements were primarily studied in inorganic and physical chemistry. However, organic derivatives of lanthanides are now drawing increasing attention as reagents for organic synthesis [1, 2].

The reactions of PhLnI* (Ln = Yb, Eu, Sm, Ce), prepared in situ according to the method in [3] in oxidative addition of PhI to a zero valence metal in THF, with α,β-unsaturated ketones (trans-chalcone and benzalacetone) and with 9-fluorenone and benzophenone were examined in the present article. It was of interest to compare the regional selectivity of addition of PhLnI to the enones with similar reactions of PhMgX and PhLi.

We note that the existence of an induction period (10-30 min) was previously observed [2, 3] in oxidative addition of PhI to Ln. We showed that the reaction begins immediately on addition of PhI after preliminary activation of the lanthanide with an insignificant amount of CH_2I_2 (~ 0.5-1 mole %).

The regiospecificity of addition of organometallic compounds to enones is known to be a function of both the nature of the reagents and the conditions of the reaction (solvent, temperature) [4-6]. The reaction of PhLi

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* The structure of PhLnI is conventionally represented in [3].

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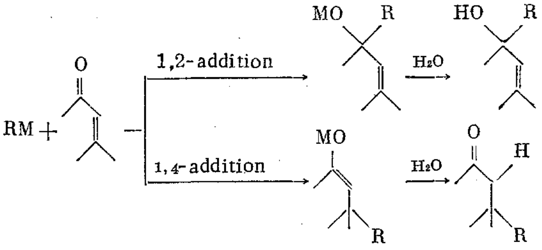
Addition of Phenyl Derivatives of Lanthanides, Mg, and Li to Trans-Chalcone in THF (−40°C, 40 min)

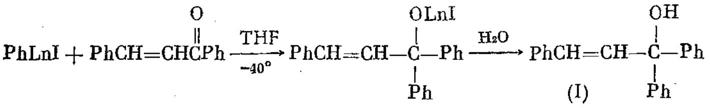
Reagent	Type of addition	Yield, %	Reagent	Type of addition	Yield, %
PhYbI	1,2	70–80	PhLi	1,2	75
PhEuI	1,2	50–60		1,4	15
PhSmI	1,2	60–70	PhMgI *	1,4	90
PhCeI	1,2	55–65			

* 20°, 3 h.

in ether with cis-chalcone occurs like 1,4-addition, while the reaction with trans-chalcone takes place like 1,2-addition [7, 8]; PhMgBr in ether is added to trans-chalcone exclusively in the 1,4 position [9]. Addition of PhLnI can thus in principle take place in two directions



It was found that the reaction of PhLnI with chalcone in THF at −40°C results in formation of a product of 1,2-addition alone (Table 1)



$$\mathrm{PhLnI} + \mathrm{PhCH{=}CH}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{Ph} \xrightarrow[-40^\circ]{\mathrm{THF}} \mathrm{PhCH{=}CH}{-}\underset{\mathrm{Ph}}{\overset{\mathrm{OLnI}}{\mathrm{C}}}{-}\mathrm{Ph} \xrightarrow{\mathrm{H_2O}} \mathrm{PhCH{=}CH}{-}\underset{\mathrm{Ph}}{\overset{\mathrm{OH}}{\mathrm{C}}}{-}\mathrm{Ph}$$

(I)

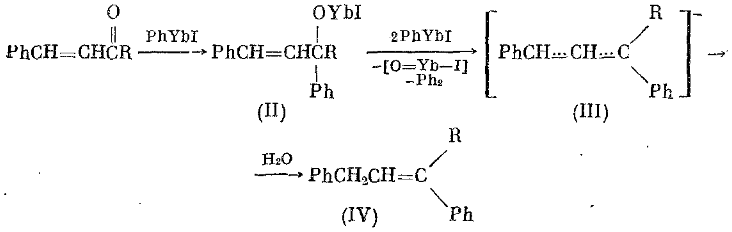
Ln = Yb, Eu, Sm, Ce

It is important that the yield of alcohol (I) is a function of the order of combining the reagents. In the usual order of addition (the ketone to a solution of PhLnI), the yield of (I) is 50-70%, while it is 60-80% in the reverse order (all yields in the article are reported with respect to the starting carbonyl compound which is totally consumed during the reaction). We note, however, that the ratio of the products of 1,2- and 1,4-addition can be a function of the nature of the R in RLnI, as [1] suggests. In the reaction of $CH_2=CHCH_2I$ with trans-chalcone in the presence of amalgamated Ce at 0°C, only an alcohol (the product of 1,2-addition) was obtained with a yield of 70%, while a mixture of ketone (1,4-addition) and alcohol in the ratio of 1:1 was obtained in the similar reaction with $PhCH_2I$.

For comparison, we conducted the reactions of chalcone with PhMgI at 20°C and PhLi at −40°C in THF. As the data obtained (Table 1) show, the selectivity of the reaction of PhLnI with chalcone differs from the selectivity observed in the reaction of PhMgI, where the product of 1,4-addition is exclusively formed according to our data and the data in the literature [9], and from the reaction of PhLi, where a saturated ketone (1,4-addition) is present in the products of the reaction in addition to (I). Unfortunately, it is not possible to compare the reactions of PhMgX and PhLnX at the same temperature, since increasing the temperature above −40°C results in the appearance of secondary products. However, heating of ytterbium diphenylstyrylcarbinolate previously prepared at −40°C to ~ 20°C does not result in the appearance of any product of 1,4-addition, which might have occurred in changing from kinetic to thermodynamic control.

The data obtained for the series of phenyl derivatives of lanthanides do not permit forming any conclusions concerning their relative reactivity in the reaction examined, since the yields of the product of addition differ insignificantly. Nevertheless, in repeated reproduction of the experiment, the highest yield of (I) was always observed for PhYbI.

An unexpected result was obtained in conducting the reaction of chalcone with an excess of PhYbI at ~ 20°C. After hydrolysis of the reactive mixture, the olefin $Ph_2C=CHCH_2Ph$, with a 60% yield, and a small amount of diphenyl were separated. During the reaction, the solution turned an intense dark red characteristic of the carbanion $[\mathrm{Ph_2C \ldots CH \ldots CHPh}]^-$ [10]. $\mathrm{Ph(CH_3)C{=}CHCH_2Ph}$ was separated with a yield of 66% in a similar reaction with benzalacetone. A mechanism consisting of 1,2-addition of PhYbI and subsequent reduction of the alcoholate formed by an excess of phenyl ytterbium iodide to a carbanion whose protonation is accompanied by migration of the double bond is the most probable



$$\mathrm{PhCH{=}CHC(O)R} \xrightarrow{\mathrm{PhYbI}} \underset{(II)}{\mathrm{PhCH{=}CHC(OYbI)(Ph)R}} \xrightarrow[-[\mathrm{O{=}Yb{-}I}],\ -\mathrm{Ph_2}]{2\mathrm{PhYbI}} \underset{(III)}{\left[\mathrm{PhCH \cdots CH \cdots C(R)Ph}\right]^-} \rightarrow \xrightarrow{\mathrm{H_2O}} \underset{(IV)}{\mathrm{PhCH_2CH{=}C(R)Ph}}$$

R = Ph (a); $\mathrm{CH_3}$ (b).

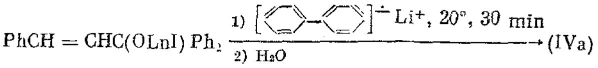
This mechanism of the reaction is confirmed by the reaction of the alcoholate previously prepared from equimolar amounts of PhYbI and chalcone at −40°C with an excess of phenyl ytterbium diodide at ~ 20°C. After hydrolysis of the reactive mixture, (IVa) is separated with a yield of 90% with respect to the starting alcoholate. The possibility of spontaneous rupture of the C−O bond is excluded, since alcoholate (IIa) is stable in THF at ~ 20°C in the absence of a reducing agent, as noted above.

Formation of carbanion (IIIa) is confirmed by its reaction with $\mathrm{CH_3I}$. The product of methylation, separated with a yield of 55% (methylation of the carbanion takes place with an almost quantitative yield, since olefin (IVa) is formed in this reaction with a yield of 60%) has the structure $\mathrm{Ph_2C{=}CHCH(CH_3)Ph}$, which is in agreement with the data in [10] on the methylation of this anion, obtained by the action of $\mathrm{NaNH_2}$ on 1,1,3-triphenylpropene.

There is a certain analogy between the deoxygenation of alcoholate (II) and the data in the literature on the transformation of epoxides into olefins under the effect of $\mathrm{SmI_2}$ or $\mathrm{YbI_2}$ [11] or $\mathrm{TiCl_3}$ in the presence of $\mathrm{LiAlH_4}$ [12]. We note that alcoholate (II) does not react with $\mathrm{YbI_2}$. This fact, as well as the formation of diphenyl during the reaction, indicates that deoxygenation is the result of reduction under the effect of the phenyl anion.

Reduction of the alcoholate under the effect of an excess of PhLnI is not only observed for derivatives of Yb, but also for Eu and Sm compounds. However, reduction does not take place when the temperature of the reaction is −40°C. In this case, only formation of alcohol (I) is observed after hydrolysis (see Table 1). When the temperature is increased to ~ 20°C and the reactive mixture is mixed for 3 h and then hydrolyzed, formation of olefin (IVa) is observed, the yield is a function of the type of lanthanide and is 70–75% for Yb and 8–12% for Eu and Sm. No olefin is formed in the reaction of PhCeI. This difference could be due to the different reducing capacity of PhLnI. On the other hand, it is necessary to bear in mind that the solution obtained in the reaction of PhI and Yb contains 86% bivalent Yb compounds, while the proportion of the compound containing $\mathrm{Sm^{2+}}$ in the similar reaction with Sm is decreased to 50% [3]. The concentration of PhLnI will thus affect both the transformation of the starting carbonyl compound into an alcoholate and the deoxygenation reaction.

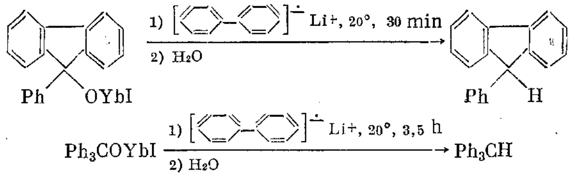
We showed that quantitative transformation into olefin (IVa) takes place with the action of a stronger reducing agent than PhLnI, lithium diphenyl, on the Ln-alcoholate of diphenylstyrylcarbinol (Ln = Yb, Eu, Sm, Ce) The yields were 70–75% for Yb, 55–60% for Eu, 65–70% for Sm, and 60–65% for Ce, which corresponds to the yields of the alcoholates formed (see Table 1)



$$\mathrm{PhCH{=}CHC(OLnI)Ph_2} \xrightarrow[2)\ \mathrm{H_2O}]{1)\ [\ldots]^{\dot{-}}\mathrm{Li^+},\ 20^\circ,\ 30\ \mathrm{min}} \mathrm{(IVa)}$$

It thus follows that the low yields of olefin (IVa) in reactions with PhEuI and PhSmI, as well as the absence of the olefin in the case of PhCeI are due to the poor reducing capacity of these phenyl derivatives. On the other hand, it is also possible that the alcoholates of trivalent lanthanides, whose deoxygenation requires preliminary reduction of the metal and consequently a stronger reducing agent, partially participate in these reactions.

Addition of PhYbI to 9-fluorenone and benzophenone was investigated to demonstrate the general nature of the deoxygenation reaction. 9-Phenyl-9-fluorenol and triphenylcarbinol were obtained with yields of 70 and 65%, respectively. Reduction of the ytterbium alcoholates of these alcohols with a three-fold excess of lithium diphenyl resulted in 9-phenylfluorene and triphenylmethane with an almost quantitative (with respect to the alcoholate) yield



Reduction of triphenylcarbinolate takes place much more slowly than reduction of the 9-phenyl-9-fluorenol alcoholate, which is in agreement with the greater stability of the 9-phenylfluorenyl carbanion. We note that the transformation found could also be of interest in synthesis, judging by the reaction for obtaining 9-phenylfluorene.

On the whole, different factors can affect the course of the deoxygenation reaction, for example: a) the capacity to reduce the organic part of the alcoholate, formed as a result of addition of PhLnI to the carbonyl group, to a stable anion; b) the valence state of the lanthanide in the alcoholate; c) the strength of the reducing agent; d) the affinity of the lanthanide for oxygen; e) the capacity of the lanthanide to change the valence state.

The varying behavior of the lanthanide and nontransition metal carbinolates thus results in the fact that addition of organometallic compounds to carbonyl compounds can take place with formation of different products: hydrocarbons and alcohols.

EXPERIMENTAL

The phenyl derivatives of the lanthanides were synthesized by the method in [3] with preliminary activation of the metal in THF by addition of 0.5-1 mole % CH_2I_2. The reaction of the PhLnI obtained with the carbonyl compounds were conducted in an atmosphere of dry Ar. The THF was purified by boiling over Na/benzophenone and was distilled immediately before the reaction. The course of the reaction was monitored by TLC. In all of the experiments, the reactive mixture was treated at the temperature of the reaction in the following manner: The mixture was poured in 40 ml of H_2O, extracted with ether, and dried over Na_2SO_4. After distillation of the solvent, the residue obtained was preparatively separated by column chromatography on Chemapol (40-100 μm) silica gel. Hexane was used to separate the hydrocarbons, and a hexane–ether system, 4:1, was used to separate the alcohols.

GLC was conducted on a Tsvet-110 chromatograph with a flame-ionization detector, He as the carrier gas, and a 1.5 m (steel) column with 3% SE-30 on N-super Chromatone. The PMR spectra were taken on a Tesla BS-497 spectrometer in a solution of CCl_4 with TMS as the standard.

Reaction of PhLnI with trans-Chalcone. a) A solution of 3 mmoles of chalcone in 10 ml of THF was added to a solution of PhLnI (Ln = Yb, Eu, Sm, Ce) prepared from 3 mmoles of PhI and 3.5 mg·at of Ln in 30 ml of THF at −40°C and mixed at −40°C until the chalcone disappeared (TLC, 40 min). Diphenylstyrylcarbinol (I), mp 110-112°C, was separated (compare [7]), 70% yield for Yb, 50% for Eu, 60% for Sm, and 55% for Ce. The reactions were conducted in similar conditions with the reverse order of combination of the reagents. The yield of (I) was 80% for Yb, 60% for Eu, 70% for Sm, and 65% for Ce.

b) A solution of 2 mmoles of chalcone in 10 ml of THF was added at ~ 20°C to a solution of PhYbI prepared from 6 mmoles of PhI and 7 mg·atom of Yb in 30 ml of THF and mixed until the reaction ended (TLC, 3 h). Separation of 1.2 mmole (60%) of 1,1,3-triphenylpropene (IVa) was obtained, and the melting point and PMR spectrum coincided with [10]. In a parallel experiment, 1.1 mmole (55%) of 1,1,3-triphenyl-1-butene was separated after treatment of the reactive mixture with 4 mmoles of CH_3I; the boiling point and PMR spectrum coincided with the data in the literature [10].

c) A solution of 2 mmoles of chalcone in 10 ml of THF at −40°C was added to a solution of PhLnI (Ln = Yb, Eu, Sm, Ce) prepared from 6 mmoles of PhI and 7 mg·atom of Ln in 30 ml of THF and mixed at −40°C until the reaction ended (TLC, 40 min). (I) was separated with a yield of 70% for Yb, 50% for Eu, 60% for Sm, and 55% for Ce. In a parallel experiment, the temperature was increased to ~ 20°C after the chalcone disappeared, and mixing was conducted for 3 h. After hydrolysis, the yield of (IVa) was determined by GLC based on an internal standard: 70-75% for Yb and 8-12% for Eu and Sm. The olefin was not found in the reaction with PhCeI.

Reaction of Benzalacetone with PhYbI with an Excess of the Organometallic Compound. A solution of 2 mmoles of benzalacetone in 10 ml of THF was added at ~ 20°C to a solution of PhYbI prepared from 6 mmoles of PhI and 7 mg·atom of Yb in 30 ml of THF and mixed until the reaction ended (TLC, 3 h). Separation of 1.32 mmole (66%) of 2,4-diphenyl-2-butene was obtained; the refractive index and PMR spectrum were in agreement with the data in the literature [13].

Reaction of PhLi with trans-Chalcone. At −40°C, 3 ml of a 1 M solution of PhLi in ether, prepared by the method in [14], were added to 30 ml of THF. A solution of 2.5 mmoles of chalcone in 10 ml of THF was then added and mixed at −40°C until the chalcone disappeared (TLC, 40 min). Separation of 1.85 mmole (75%) of (I) and 0.38 mmole (15%) of β,β-diphenylpropiophenone, mp 91°C, was obtained (compare [7]).

Reaction of PhMgI with trans-Chalcone. A solution of 3 mmoles of PhI in 30 ml of THF was added to 4 mg·atom Mg at ~ 20°C. The mixture was mixed until the PhI disappeared (TLC). A solution of 2.5 mmoles of chalcone in 10 ml of THF was then added and mixed until the reaction ended (TLC, 3 h). Separation of 2.25 mmoles (90%) of β,β-diphenylpropiophenone, mp 91°C, was obtained.

Reduction of Lanthanide Diphenylstyrylcarbinolates under the Effect of Lithium Diphenyl. Solutions of lanthanide diphenylstyrylcarbinolates were prepared from 3 mmoles of PhLnI (Ln = Yb, Eu, Sm, Ce) and 3 mmoles of chalcone at −40°C by the method described above, using the reverse order of mixing the reagents. The temperature was then increased to ~ 20°C (the composition of the products of the reaction did not change as monitored by TLC) and 5 mg·atom of Li and 5 mmoles of diphenyl were added. The mixture was mixed at ~ 20°C until the reaction ended (TLC, 30 min). After hydrolysis the yield of olefin (IVa) was determined by GLC with an internal standard: 70-75% for Yb, 55-60% for Eu, 65-70% for Sm, and 60-65% for Ce.

Reaction of PhYbI with 9-Fluorenone and Reduction of the Alcoholate Formed by Lithium Diphenyl. A solution of PhYbI prepared from 3 mmoles of PhI and 3.5 mg·atom of Yb in 30 ml of THF was added at ~ 20°C to a solution of 3 mmoles of 9-fluorenone in 10 ml of THF and mixed until the reaction ended (TLC, 45 min). Separation of 2.1 mmoles (70%) of 9-phenyl-9-fluorenol, mp 107-109°C, was obtained (compare [15]). In a parallel experiment, 5 mg·atom of Li and 5 mmoles of diphenyl were added after the starting 9-fluorenone disappeared. The mixture was mixed at ~ 20°C until the reaction ended (TLC, 20 min). Separation of 1.95 mmole (65%) of 9-phenylfluorene, mp 141-143°C, was obtained (compare [15]).

Reaction of PhYbI with Benzophenone and Reduction of the Alcoholate Formed by Lithium Diphenyl. A solution of PhYbI prepared from 3 mmoles of PhI and 3.5 mg·atom of Yb in 30 ml of THF was added at 0°C to a solution of 3 mmoles of benzophenone in 10 ml of THF and mixed at 0°C until the reaction ended (TLC, 2 h). Separation of 1.94 mmole (65%) of triphenylcarbinol, mp 162°C, was obtained (compare [16]). In a parallel experiment, 5 mg·atom of Li and 5 mmoles of diphenyl were added after the starting benzophenone has disappeared. The mixture was mixed at ~ 20°C until the reaction ended (TLC, 3.5 h). Separation of 1.8 mmole (60%) of triphenylmethane, mp 92°C, was obtained (compare [16]).

Preparation of YbI_2. At ~ 20°C, 3 mmoles of CH_2I_2 were added to 4 mg·atom of Yb in 30 ml of THF. After the reaction ended (TLC, 15 min), a yellow-green solution was obtained; the UV spectrum and results in titration of the halide ion with $AgNO_3$ were in agreement with the data in the literature [11].

CONCLUSIONS

1. The reaction of PhLnI (Ln = Yb, Eu, Sm, Ce) with trans-chalcone takes place regiospecifically as 1,2-addition, in contrast to the reactions of PhMgI and PhLi.

2. A new reaction of deoxygenation of the lanthanide carbinolates (prepared by addition of PhLnI to ketones) under the effect of reducing agents was found.

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AMINOACYL DERIVATIVES OF NUCLEOSIDES, NUCLEOTIDES, AND POLYNUCLEOTIDES

17.* POSSIBLE USE OF N,N'-THIOCARBONYLDIIMIDAZOLE FOR SYNTHESIS OF 2'(3')-O-AMINOACYLNUCLEOTIDES

P. P. Purygin and Z. P. Laletina

UDC 542.91:547.963.3

The method of synthesis of 2'(3')-O-aminoacylnucleotides using N,N'-carbonyldiimidazole for the activation of the carboxylic group of the amino acids has been described in several papers [1-3]. The disadvantage of this method is the high sensitivity of N,N'-carbonyldiimidazole to moisture [4], so that the preparation of imidazolides of amino acids must be carried out in absolute solvents. The selective aminoacylation of the nucleotides also proceeds in an aqueous–organic medium with a water content of $> 50\%$ [5]. As the result, the amino acid imidazolides not only react with nucleotides but are also subjected to hydrolysis, and therefore 4 to 10 moles of the amino acid imidazolide per mole of nucleotide are introduced into the reaction [4]. There is only one paper in the literature on the possible use of diethyl phosphate imidazolide as an activating agent for the synthesis of 2'(3')-O-aminoacyl nucleotides in an aqueous medium [6].

Our attention was drawn to N,N'-thiocarbonyldiimidazole, which is used for the activation of the carboxyl group of amino acids in the peptide synthesis [7], as a possible condensing agent. Its half-decomposition period in an aqueous–organic medium is several hours [8].

In the present work we report on the possible use, in principle, of N,N'-thiocarbonyldiimidazole for the synthesis of 2'(3')-O-aminoacylnucleotides in an aqueous medium. The synthesis was carried out by starting from an imidazolide of N-tert-butyloxycarbonylalanine BOC-Ala-Im (III), obtained from BOC-Ala-OH (I) and N,N,-thiocarbonyldiimidazole (II) and nucleoside 5'-phosphates (IV) (scheme 1). The main studies on the selection of the condensation conditions were carried for adenosine 5'-phosphate (pA) and imidazolide (III). Compound (I) was condensed with (II) and (III) with (IV) in water at ~20°C. The initial nucleotides were introduced into the reaction in the form of a disodium or diammonium salt. Determination of the yields of 2'(3')-O-BOC-alanylnucleotides depending on the time of reaction showed that the highest yields are obtained after 2.5 h and are 15-20% (Table 1). Imidazolide (III) was taken in excess with respect to nucleotide (IV). The above yields were obtained at a ratio (III) : (IV) = 10:1 (moles). Further increase in this ratio does not influence the yield of 2'(3')-O-BOC-alanylnucleotides (V).

The isolation, purification, and verification of the structure of 2'(3')-O-BOC-alanyl-pA (V), 2'(3')-O-alanyl-pA (VI) were carried out by chromatography, electrophoresis, and UV spectroscopy (Table 2).

The absorption maxima in the UV spectra of the initial compounds (IV) and esters (V) and (VI) are located at the same wavelength, while the electrophoretic mobility of (VI) at pH 2.5 corresponds to the number of charges on it, which indicates the absence of acylation of the heterocyclic bases.

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*Article 16, see [1].

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