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## REACTIONS OF DIPHENIC ACID WITH CARBAMIDE AS A WAY TO ACYCLIC AND CYCLIC AMIDES OF DIPHENIC ACID

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*On the basis of reaction of diphenic acid with carbamide in the conditions of azeotropic water distillation a new way of producing acyclic and cyclic amides of diphenic acid has been found. The nature of amidating agent is shown to determine composition of reaction products: at amidating diphenic acid not substituted by carbamide the basic product is imide, whereas at amidating by substituted carbamide and amines it is corresponding monoamide. On the basis of experimental data the mechanism of the reactions is suggested.*

Imides of diphenic (2,2'-diphenyldicarboxylic) acid (DA) attracts attention first of all as initial substrates for synthesis of new bioactive compounds with dibenz [c,e] azepine structure [1].

Substituted mono- and diamides of DA with relatively high yields (70...80 %) are obtained by means of classical method at straight acidation of corresponding amine with diphenic anhydride II [2] or with dichlorine anhydride [3] respectively. In paper [2] the method of obtaining of substituted diamides and imides of DA from the acid I itself and corresponding amines in the presence of  $\text{PCl}_5$  in xylene medium is also presented. Only one preparatively meaningful method of synthesis of unsubstituted monoamide IIIa and imide of DA IVa is described in scientific literature. This method consists in obtaining its anhydride II from DA I, then monoamide IIIa and its further cyclization into imide IVa [4, 5] (scheme 1).

Finite yield of imide IVa obtained by this method is not more than 65...70 % (in terms of initial DA I), and total time of three chemical stages is 9,5 h., nonmetering extraction and purification procedures.

Thus, existing preparative methods of synthesis of above-named compounds differ in multistaging or using inaccessible and high-toxic agents.

The method of obtaining cyclic imides from dicarboxylic acids and their anhydrides in carbamides melts is rather known [6]. However, when obtaining imides with cycle size more than 6 links, this method is not always suitable owing to low selectivity and low yields of desired products. Really, it has been found out that at interaction of DA I with carbamide in melt imide IVa is formed with yields not exceeding 15...20 %.

Therefore, the problem of searching for new preparative methods of synthesis of DA imides, distinguished

by single-staging, substrates and agents accessibility, and also high yields of desired products occurs.

Previously, the new handy method of synthesis of DA unsubstituted imide IVa [7] was suggested. The essence of this method consists in DA I amination with carbamide or formamide, in the indifferent organic solvent not mixed with water and formed azeotropic mixture with it. Water formed in the course of reaction is distilled with solvent, in which the reaction is carried out, with solvent return into reaction mass after water separation. To carry out the described process high-boiling organic solvents of aromatic series, such as *o*- and *n*-xylenes were used.

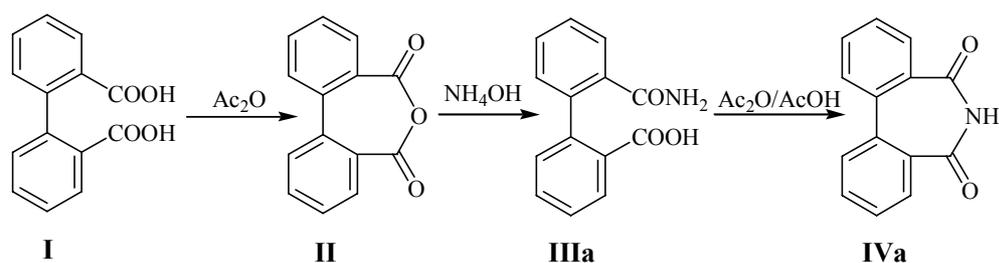
To expand the developed method preparative abilities, and also to find out regularities of reactions we have investigated DA I amination in the conditions [7] with certain N,N'-disubstituted carbamides, N-monosubstituted carbamides, initial alkyl-, arylamines, and also with the same initial amines, but in the presence of carbamide (scheme 2).

Experimental data on dependence of products yields and reaction time on nature of amidating agent and molar ratio agent:DA are presented in table 1.

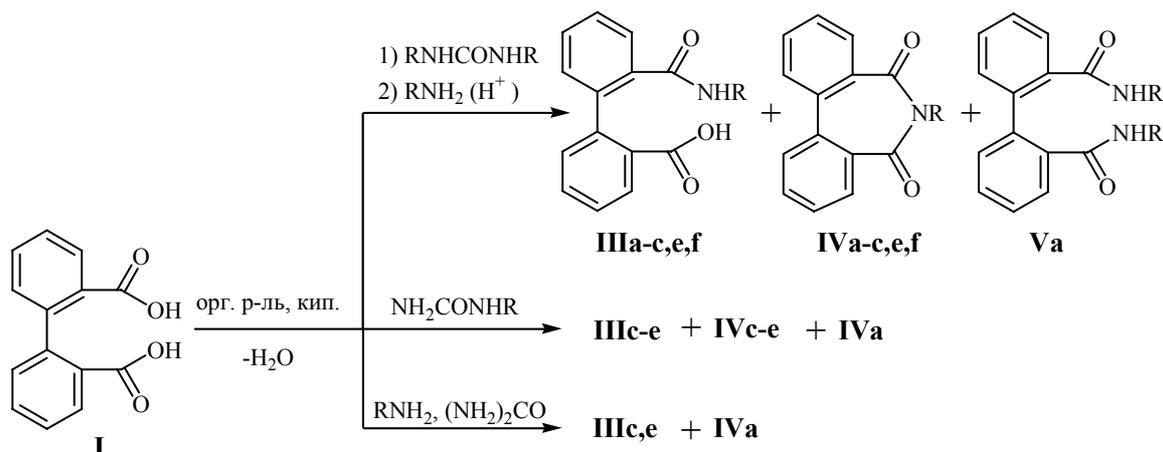
The analysis of data of the table shows that:

1. Nature of amidating agent determines the composition of reaction products. So at amination of DA I with unsubstituted carbamide the main reaction product is imide IVa, and at amination with substituted carbamides and amines it is corresponding monoamides III b-f.
2. Molar ratio amidating agent:DA influences substantially the reaction products yield.
3. DA I amination with free initial amines occurs more difficult than with their derivatives with carbamide,

**Scheme 1**



Scheme 2



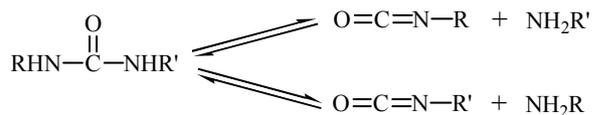
where R=H(a), CH<sub>3</sub> (b), Ph (c), *n*-Bu (d), CH<sub>2</sub>Ph (e), 1-naphthyl (f)

in this case addition of acid catalyst (*n*-toluene sulfonic acid) into reaction mass influences practically neither the reaction rate nor products composition.

The obtained experimental data allow us to suppose that DA imides **IVa-f** formation occurs through the medium formation of monamides **IIIa-f**. At DA **I** amination with carbamide the rate of formation of monamide **IIIa** is significantly lower than the rate of its cyclization into imide **IVa**, therefore concentration of monamide **IIIa** in reaction mass is rather low independently of reaction time. In a single experiment it was showed that monamide of DA **IIIa** obtained independently in the presence of equimolar quantity of carbamide in the stated conditions passes completely into imide **IVa** during 3 hours. In the absence of carbamide only formation of trace quantities of imide **IVa** is observed during 10 hours of reaction. For substituted carbamides the inverse is observed – formation of monamide **IIIb-e** occurs faster than its cyclization into imide **IVb-e**, therefore this product may be extracted in considerable quantities (to 80...85 %). However, as it is seen from table 1 (№ 13), if the process is not stopped at the stage of obtaining substituted monamide **IIIb**, then the corresponding imide **IVb** is formed.

Let us consider the first stage of the process, i.e. the formation of DA monamides **IIIa-e**. It is known that both carbamide itself and its substituted derivatives at high temperatures dissociate according to the scheme

Scheme 3



The process has a reversible nature and its relative velocity in each direction depends on substituents nature [8, 9].

Thus, carbamide dissociation results in formation of two types of nitrogen-containing compounds, each of which may be amidating agent. Taking into consideration the fact that nitrogen atoms in carbamides are much

weaker nucleophils than in antecedent amines owing to conjugation with carbonyl group, we do not consider the variant when carbamide itself becomes amidating agent.

It is shown that free amines even in the presence of acid catalysts react with DA **I** considerably slower than carbamides, containing similar substituents (table 1). Therefore, though that direction of the reaction in which immediate attack of carboxyl group by amine nitrogen is possible, but it is not dominant and is ignored in further discussion of the mechanism.

The assumption that carboxylic acids amination with carbamides occurs through the initial attachment of isocyanate, formed from carbamide, to carboxyl group of acid was repeatedly stated in scientific literature [10]. Taking into account high reactivity of isocyanic acid and isocyanates, such assumption seems to be obvious.

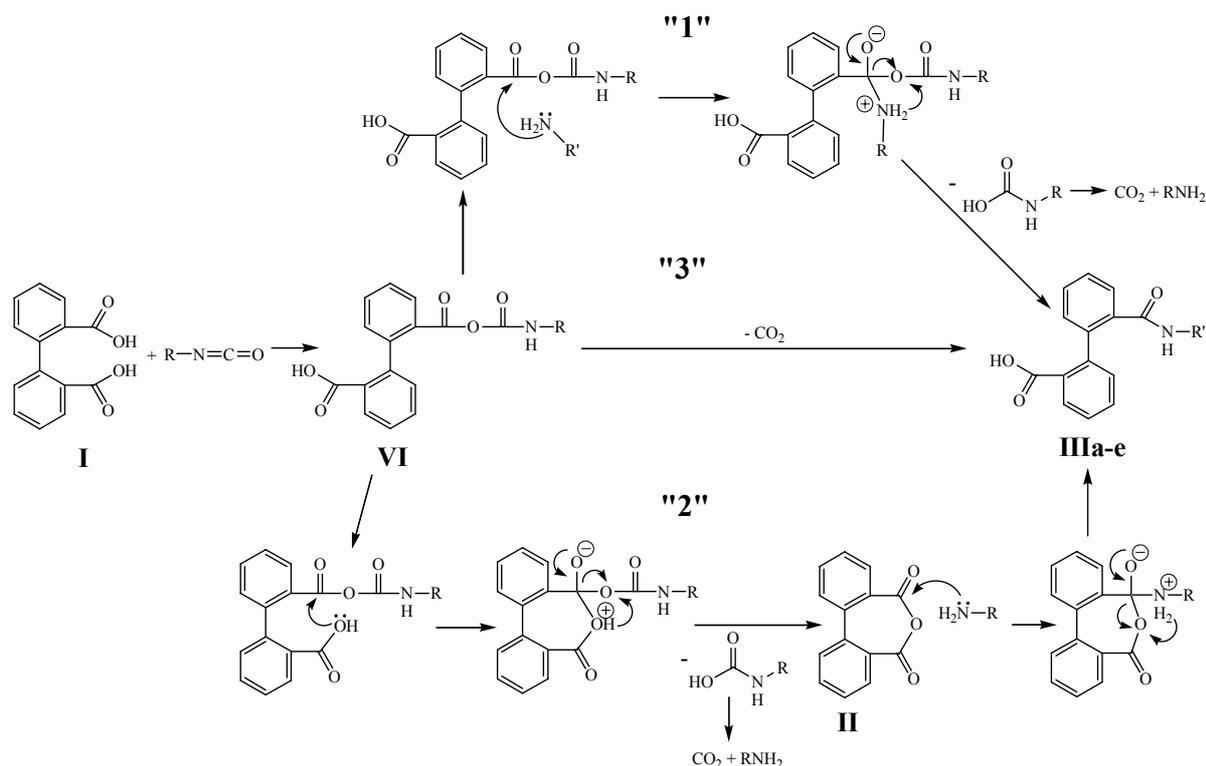
In our case, the attachment of one molecule of isocyanate to one carboxyl group of DA **I** at the first stage of the reaction should result in formation of acylurethane **VI** (scheme 4). Three probable directions of further transformations of intermediate acylurethane **VI**, resulting in formation of monamide of DA **IIIa-e** were examined and they are presented in scheme 4.

The direction «1» seems to be rather probable as such well displaced group as carbamic acid, which easily breaks down to CO<sub>2</sub> and amine, is displaced by the molecule of amine. So the given process should be practically irreversible.

Another possible direction of further transformations of intermediate acylurethane **VI** (direction «2») is its cyclization into anhydride of DA **II** with ejection of a molecule of carbamic acid, like in the first case. Then the amine acidulating with formed anhydride **II** occurs, resulting in obtaining monamide **IIIa-e**.

The process of amination in the directions «1» and «2» does not contradict to known ideas about mechanisms of such reactions [11]. However, if one supposes the dominance of these directions in our case, then at DA **I** amination with monosubstituted carbamides one

Scheme 4



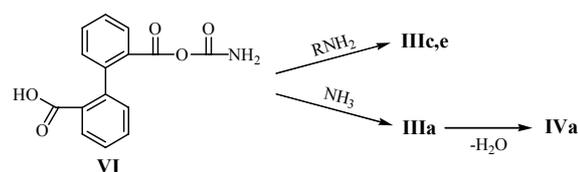
should expect the formation of a mixture of unsubstituted imide **IVa** and corresponding substituted monamides **IIIc-e** with the dominance of that product which amine with more expressed nucleophilic properties conforms to. In view of the fact that both of these directions imply competitive attack of intermediate acylurethane **VI** or anhydride **II** by the molecules of two different amines, then, for example, in the case of *N*-phenylcarbamide the dominant reaction product should be unsubstituted imide **IVa** (as ammonia is much stronger nucleophil than aniline). And in the case of benzyl- or *n*-butylcarbamide, on the contrary, the dominant product is substituted by monamide **IIIc,e** (here the nucleophilic property of ammonia is weaker than that of corresponding amines). Even if one supposes that initial monosubstituted carbamide dissociates exclusively isocyanic acid and amine, i.e. it does not form free ammonia on this stage, then the latter should be unavoidably accumulated in the reaction mass at the following stages of the process and namely after decomposition of carbamic acid. Really, regardless of nucleophilic properties of amines in all presented cases, the formation of mostly substituted monamides **IIIc-e** is observed, but unsubstituted imide **IVa** presents in reaction products only in very small quantities.

By aminating DA **I** with initial amines in the presence of carbamide the process of competitive attachment of amines to intermediate compound **VI** was simulated (scheme 5).

If one supposes that acylurethane **VI** formed from DA **I** and isocyanic acid may be subjected to the competitive attack by both ammonia, appeared as a result of

carbamide dissociation and amine, presenting initially in a small quantities in the reaction mass, then it is obvious that the ratio of formed amides **IIIa** or **IIIc,e** will be determined by the ratio of concentrations of amine and ammonia and also by their nucleophilic properties. The results of amination with aniline in the presence of carbamide conform with the presented scheme 5. However, when aminating with benzylamine, one should expect the opposite effect. Taking into consideration higher nucleophilicity of benzylamine in comparison with ammonia, and also the fact that ammonia concentration is always lower than that of benzylamine in the course of reaction, then according to the given scheme, benzylamide **IIIe** should be expected as the main product of the reaction. Thus, the obtained experimental data allow declining with significant degree of confidence the variants of DA **I** amination, occurring through the attachment of amine (ammonia) to acylurethane **VI**.

Scheme 5



where R = Ph (c), CH<sub>2</sub>Ph (e)

The observed formation of a number of amides **IIIc,e** may be explained by the reaction of DA **I** with substituted carbamides, which are formed simultaneously *in situ* from carbamide and amines.

**Table 1.** Dependence of reaction products yields and time on nature of amidating agent and molar ratio agent:DA (solvent-*n*-xylene)

№	Amidating agent	R	R'	Quantity of amidating agent moles per DA mole	Time, h	Yield, %									
						III	IV	V							
1	RNHCONHR'	H	H	0,5	3,5		30	<1							
2				1	4		86	3							
3				1,5	4	<1	62	5							
4				4	4,5		22	10							
5				8	5,5		7	20							
6		H	H-Bu	1	4,5	67	3 (IVa) 3 (IVd)								
7				2	5	78	6 (IVa) 1 (IVd)								
8			Ph	1	5	72	4 (IVa) <1 (IVc)	-							
9				2	7,5	75	5 (IVa) <1 (IVc)								
10		RNHCONHR'	CH <sub>3</sub>	CH <sub>3</sub>	1	7	77	4 (IVa) 1 (IVe)							
11	Ph									Ph	1	6	50	5	<1
12											2	5	66	4	
13											2	25*	58	14	
14											4	3,5	80	2	
15			8	3	87	1									
16	Ph		Ph	0,75	6,5	60	<1	-							
17				1	7,5	77									
18				2	9	79									
19				4	12	81									
20	RNH <sub>2</sub>	Ph	-	2	25**	33	1,5								
21									30**	9	traces				
22									30**	12	traces				
23									25**	36	2				
24	RNH <sub>2</sub> , catalytic quantities TsOH	CH <sub>2</sub> Ph	-	2	30**	14	traces	-							
25									Ph	7	64	7 (IVa)			
26	Equimolar mixture RNH <sub>2</sub> and (NH <sub>2</sub> ) <sub>2</sub> CO	CH <sub>2</sub> Ph	-	1	6,5	55	10 (IVa)								

\*Reaction was continued after DA complete reacting

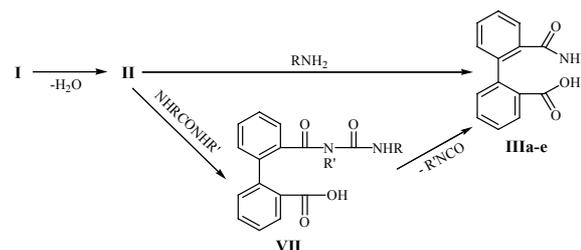
\*\*Unreacted DA remained

The obtained experimental data suggest that amine fragment, presenting after that in the structure of monamide **IIIa-e** and imide **IVa-e**, enters not by means of amines attachment to intermediate compound **II** or **VI** formed from AD **I**, but at the stage of isocyanate attachment to the molecule of DA **I**. After that, as a result of intramolecular rearrangement CO<sub>2</sub> is ejected from

acylurethane **VI** and corresponding amide **IIIa-e**, containing the same substituent as the initial isocyanate, is formed (direction «3», scheme 4). Such reactions, resulting in obtaining amides from additive compounds of isocyanates to carboxyl groups are known by the examples of monocarboxylic acids [10, 11].

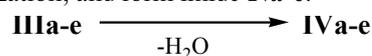
One more variant of monamide **IIIa-e** formation may be supposed, when initial DA **I** firstly turns into anhydride **II** which then reacts with amine, formed from carbamide, or directly with carbamide (scheme 6).

**Scheme 6**



However, the fact that DA **II** anhydride was never found either in reaction mass or in reaction products and also the fact that a separate DA **I** does not turn into anhydride **II** in the conditions of azeotropic distillation allow rejecting this supposition. These data are also the additional arguments against amination in the direction «2» (scheme 4).

Monamide of DA **III a-e**, formed at the first stage, is in the sequel undergone dehydration, accompanied wby cyclization, and form imide **IVa-e**.



The acceleration of this reaction in the presence of acids was stated. So monamides **IIIa-c, e** in the absence of acid in the conditions of azeotropic water distillation form the corresponding imides **IVa-c, e** only in trace quantities, whereas in the presence of acid catalyst (*n*-toluol sulfonic acid) monamide of DA **IIIa** completely turns into imide **IVa** during 20...30 min., *N*-methylamide **IIIb** – during 2 h; *N*-phenyl- and *N*-benzylamides **IIIc,e** – during 10 h turn into imides **IVc,e** only by 40 and 55 % correspondingly. These data may point to the fact that steric effects of substituents influence essentially the rate of dehydration.

At carbamide dissociation, isocyanic acid is formed which is known as relatively strong acid, therefore it may serve as a catalyst of dehydration of monamide **IIIa**.

The fact that at DA **I** amination with carbamide, unlike its substituted derivatives, monamide **IIIa**, formed intermediately, turns easily into imide **IVa** is explained by these suppositions.

Imides **IVa-c, e** and monamides **IIIa-e** were obtained in oncoming synthesis by the method, given in [5] from DA **II** anhydride and corresponding amines. Characteristics of all compounds, obtained in oncoming synthesis, coincide completely with the characteristics of the compounds, obtained by the method developed.

## Experimental

Control on the reaction and identity of obtained compounds was carried out with the help of thin-layer chromatography on the «Sorbfil» ПТТСХ-АФ-В-УФ plates, eluent is benzole-ethanol (4:1 by volume), detection of spots by UV-light (254 nm), and also by termination of water release from condensate of azeotropic mixture. At DA I amination with such soft carbamides as unsubstituted carbamide, N,N'-dimethyl carbamide, N-butyl carbamide the process termination may be also judged by disappearance of corresponding carbamide melt from the reaction mass.

Spectra of proton magnetic resonance were obtained at the spectrometer Avance-300 (300 MHz), internal standard is ГМДС, solvent is CDCl<sub>3</sub>. IR spectra were obtained at the devices Avatar Nicolett 5700 and Specord IR-75 in KBr tablets.

The characteristics of synthesized compounds are presented in table 2.

**General technique of DA I amination with unsubstituted carbamide.** Calculated quantity of DA I and carbamide are loaded into one-necked flask provided with Din-Stark head with backflow condenser. Solvent (xylene) is added in terms of 50...60 ml per 1g of DA I. The reaction mixture is boiled during 3, 5...5 h at 138 °C. After that, the reaction mixture is cooled step-by-step to 20...25 °C and stayed for 10...12 h. The sediment of imide **IVa**, lade-down in the form of colorless needles is filtered and dried. Distilling the solvent off the filter, it is regenerated and the residuals of imide **IVa** being isolated. Both portions of the product are combined, treated with 5 % solution of sodium carbonate, then dissolved in excess of 7 % solution of NaOH. The obtained solution is filtered; filtrate is treated with diluted hydrochloric acid to subacid medium reaction. The lade-down sediment of imide **IVa** is filtered, washed on a filter with water excess and dried. At neutralization of carbonate solution the sediment of monamide **IIIa** is obtained which is also filtered and dried. The sediment on the filter after washing with NaOH solution is boiled in iso-

propyl alcohol during 10...15 min. and filtered. Solvent is distilled off the filter, fixed residue is dried, diamide of DA **Va** is obtained. The obtained imide **IVa** is precrystallized from acetonitrile, monamide **IIIa** and diamide **Va** are done from acetic acid.

**General technique of DA I amination with N – substituted carbamides.** Carrying out of the synthesis is similar to the amination with unsubstituted carbamide, however, in this case less quantity of solvent (30...40 ml per 1g of DA I) may be used. After the reaction Din-Stark head is exchanged by straightforward condenser and approximately 2/3 of solvent is distilled off. The residual in the flask is cooled to 20...25 °C (in this case oil or solid residual precipitation is possible) and poured with excess of 5 % solution of sodium carbonate. The obtained mixture is thoroughly shaken to sediment (oil) complete dissolution and after that it is separated at separating funnel. Water layer is neutralized with diluted hydrochloric acid; monamide **IIIa-e** is precipitated, filtered, washed on a filter with excess of water and dried. With the organic layer depending on the type of used carbamide is treated in the following way: a) at amination with N- substituted carbamides the organic layer is firstly treated with 7 % solution of NaOH, which is then separated and neutralized with the solution of HCl and so unsubstituted imide **IVa** is obtained. Then xylene is distilled off the organic layer under pressure of 10...20 kPa, fixed residue is precrystallized from isopropyl alcohol and substituted imide **IVa-e** is obtained; b) at amination with N,N'-disubstituted carbamides the organic layer treatment with alkali solution is not required. The obtained substituted monamides **IIIa-e** are precrystallized from the mixture acetic acid-water (1:1 by the weight), imide **IVa** – from acetonitrile, imides **IVa-e** – from isopropyl alcohol.

## Conclusion

Thus, the new way of acyclic and cyclic amides of DA synthesis has been found. It is based on the reaction of DA I with carbamides in the conditions of azeotropic

**Table 2.** The characteristics of synthesized compounds

Compound	$T_{\text{melt.}}, ^\circ\text{C}$	Chemical shift, $\delta$ , m.c.				Absorption bands in IR spectrum, $\text{cm}^{-1}$	
		N-H	Ar-H	-COOH	Others	NH	CO
IIIa	198...199	6,18, d., 2H	7,15...7,81, m., 8H	11,62, s., 1H	–	3270	1600, 1660
IIIb	207...208	*	6,54...7,73, m., 8H	11,78, s., 1H	2,70, d., 3H, -CH <sub>3</sub>	3300	1600, 1680
IIIc	165...167	8,43, s., 1H	7,06...7,86, m., 13H	10,05, s., 1H	–	3240	1615, 1680
IIId	101...102	*	7,02...7,75, m., 8H	11,90, s., 1H	3,04, m., 2H, 1-CH <sub>2</sub> 1,00, m., 2H, 2-CH <sub>2</sub> 0,94, m., 2H, 3-CH <sub>2</sub> 0,69, t., 3H, -CH <sub>3</sub>	3295	1605, 1680
IIIe	155...156	*	6,77...7,71, m., 13H	11,52, s., 1H	4,34, m., 2H, -CH <sub>2</sub> Ph	3300	1605, 1710
IVa	219	12,10, s., 1H	6,50...7,12, m., 8H	–	–	–	1670, 1695
IVb	164...165	–	7,45...7,84, m., 8H	–	3,45, s., 3H, -CH <sub>3</sub>	–	1650, 1670
IVc	190	–	7,28...7,96, m., 13H	–	–	–	1655, 1690
IVe	125...126	–	7,40...7,89, m., 8H	–	5,02, m., 2H, -CH <sub>2</sub> Ph	–	1650, 1680
Va	209...210	6,24, s., 4H	7,10...7,72, m., 8H	–	–	–	–

In IR spectra of monamides **III a-e** the signals of free OH group were not found out.

\*Signals of amide protons **III b, d, e** occur under the signals of aromatic ones, therefore they were not identified

water distillation. It is shown that the nature of amidating agent determines the composition of reaction products: at amination of DA **I** with unsubstituted carbamide the main product is imide **IVa**, and at amination with substituted carbamides and amines the main products are corresponding monamides **IIIb-f**. On the basis of experimental data the mechanism of reaction is suggested.

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## PROCESS OF CATALYTIC SYNTHESIS OF ACETONITRILE FROM ACETIC ACID AND AMMONIA AT $\gamma$ - $\text{Al}_2\text{O}_3$

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*In the reaction of catalytic synthesis of acetonitrile from acetic acid and ammonia the influence of ratio of reagents, reactor temperature, addition of acetic acid, acetic anhydride and acetamide into the reaction mixture of ethyl ether as well as catalyst promotion ( $\gamma$ - $\text{Al}_2\text{O}_3$ ) by phosphoric acid on the parameters of the process. Optimal conditions of the reaction are determined and the scheme of commercial prototype process is suggested.*

Acetonitrile is widely used in organic synthesis as an intermediate reagent, solvent, azeotrope – forming at substances separation [1, 2], as well as at synthesis of  $\text{CN}_x$  nanotubes [3]. In industry acetonitrile is produced as a by-product of acrylonitrile synthesis. Processes directed at target synthesis of acetonitrile become perspective because of increasing requirement of acetonitrile in petrochemical syntheses. Methods of acetonitrile obtaining from ammonia and acetic acid, alcohols, paraffins and olefines [4] are developed. Syntheses from alcohols, paraffins and olefines are characterized by insufficient selectivity and low process productivity. Until recently none of methods of purposeful acetonitrile synthesis is realized in industry.

Synthesis of acetonitrile from acetic acid is perspective for realization owing to little consumptions for separation and purification of a target product. Well-known syntheses of acetonitrile from acetic acid and ammonia [4–6] were carried out in tubular reactors with volume velocity of acid supplying  $0,3 \text{ h}^{-1}$  or  $0,008\text{...}0,060 \text{ mole/sec}\cdot\text{l}$  acetonitrile yield higher than 80 % was observed at temperatures  $440\text{...}480 \text{ }^\circ\text{C}$ . But carrying out the reactions at above mentioned temperatures results in thermal pyrolysis of an acid and products of synthesis with catalyst carbonizing and desired product – acetonitrile- contamination, besides high expenditure of energy for reactor heating. At high temperatures formation of hydrocyanic acid is possible when using steel reactor.