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Acylpyruvic Acids Amides and Hydrazides: VIII.* Synthesis of Pivaloylpyruvamides and Their Reactions with Benzylamine and Arylamines

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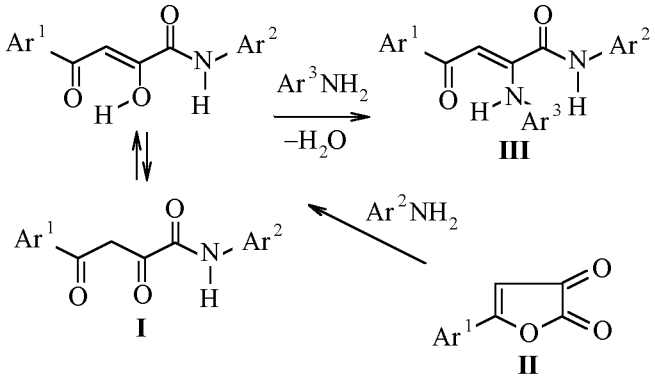
Abstract—Pivaloylpyruvamides were obtained by reaction of pivaloylpyruvic acid with ammonia, primary and secondary amines. The amides in solutions exist as an equilibrium tautomeric mixture of ketoenol and minor β-diketone forms. The pivaloylpyruvamides under mild conditions react with benzylamine or arylamines to furnish products of substitution at the α-carbonyl group, the corresponding amides of (*Z*)-2-benzylamino- or 2-arylamino-5,5-dimethyl-4-oxo-2-hexenoic acid. The latter also exist in solutions as two tautomers. The amides synthesized possess a biological activity.

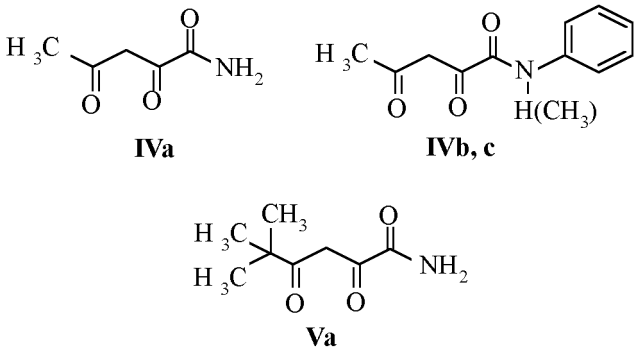
Arylamides of aroylpyruvic acids **I** obtained by decyclization of 5-aryl-2,3-dihydro-2,3-furandiones **II** effected by primary aromatic amines [2, 4] are known to react with arylamines to furnish the corresponding 2-aminoderivatives of 4-oxobutenamides **III** [5] (Scheme 1). The structure and properties of amides **III** were not previously investigated, and their alkyl analogs were poorly studied since the initial amides of aliphatic α,γ-dioxoacids were difficult to obtain before our research.

Scheme 1.

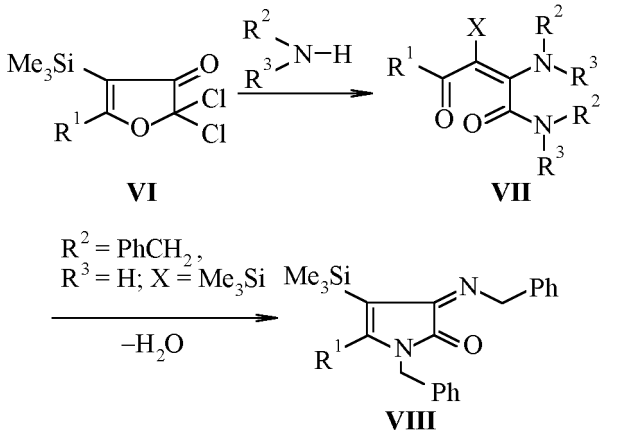


For instance, among alkanoylpyruvamides are briefly described the syntheses of amide, anilide, and *N*-methylanilide of acetylpyruvic acid (**IVa–c**) [6–9], and of pivaloylpyruvamide (**Va**) [10] in the publications dating from over a half century (Scheme 2).

Scheme 2.



Scheme 3.



VI, VII, VIII, R^1 = Bu, *s*-Bu, $PhCH_2CH_2$; **VII**, R^2 = Et, $PhCH_2$; R^3 = H, Et; X = H, Me_3Si.

* For communication VII, see [1].

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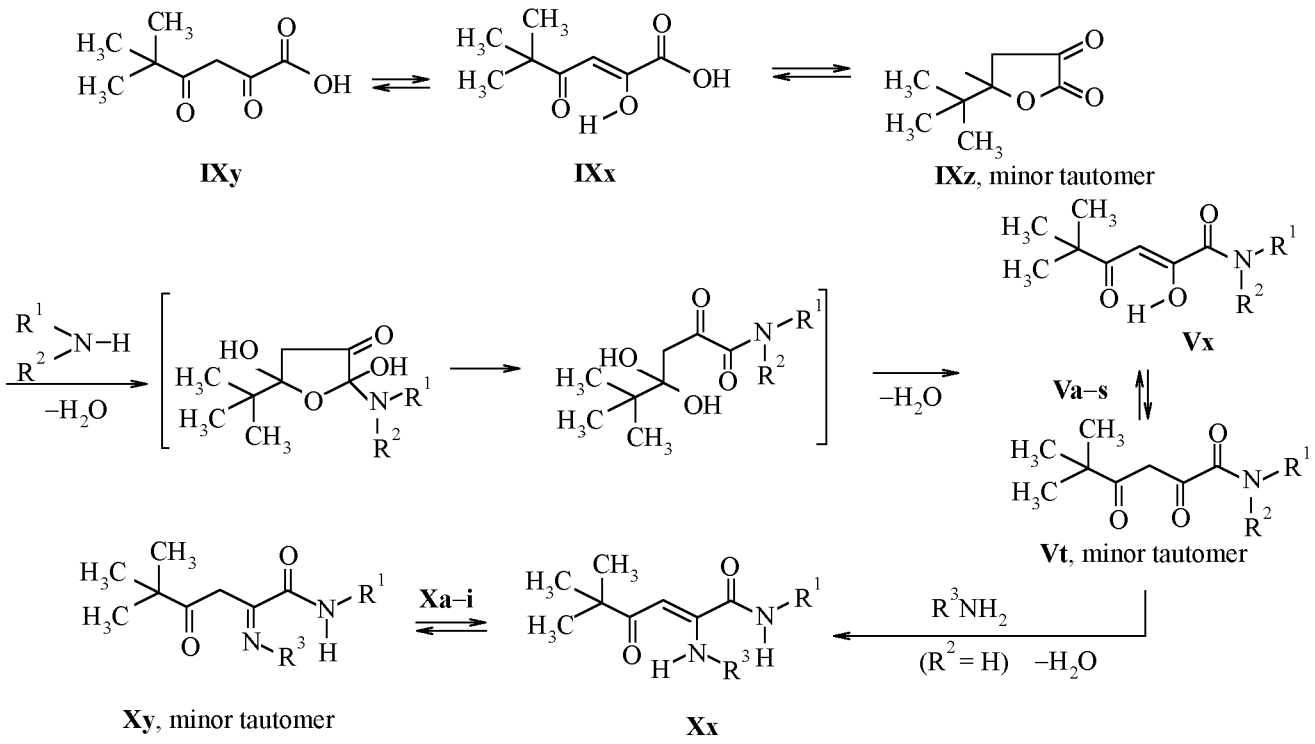
Scheme 4.



Compd. no.	R^1	R^2	Compd. no.	R^1	R^3 (R^2)
Va [10]	H	H	**Vo**	3-pyridyl	(H)
Vb	CH_3	H	**Vp**	4-pyridyl	(H)
Vc	$(CH_3)_2CH$	H	**Vq** [4]	2-thiasolyl	(H)
Vd	$(CH_3)_3C$	H	**Vr**	2-pyrimidinyl	(H)
Ve	C_2H_5	C_2H_5	**Xa**	$C_6H_5CH_2$	$C_6H_5CH_2$
Vf	cyclo-C_6H_{11}	H	**Xb**	$C_6H_5CH_2$	C_6H_5
Vg [4]	$C_6H_5CH_2$	H	**Xc**	$C_6H_5CH_2$	4-$CH_3C_6H_4$
Vh [4]	C_6H_5	H	**Xd**	$C_6H_5CH_2$	4-$CH_3OC_6H_4$
Vi [4]	4-$CH_3C_6H_4$	H	**Xe**	4-$CH_3OC_6H_4$	$C_6H_5CH_2$
Vj [4]	4-$CH_3OC_6H_4$	H	**Xf**	4-$CH_3OC_6H_4$	4-$CH_3C_6H_4$
Vk	2-$CH_3OCOC_6H_4$	H	**Xg**	2-pyridyl	C_6H_5
Vl	4-$C_2H_5OCOC_6H_4$	H	**Xh**	2-pyridyl	4-$CH_3C_6H_4$
Vm	NR^1,R^2 = morpholino		**Xi**	2-pyridyl	4-$CH_3OC_6H_4$
Vn [4]	2-pyridyl	H			

Recently was briefly reported that 5-alkyl derivatives of 2,3-dihydro-4-trimethylsilyl-2,2-dichloro-3-furanones (**VI**) similar in chemical properties to 2,3-furandiones under treatment with benzylamine and diethylamine underwent decyclization to afford in high yield substituted (*E*)-2-amino-4-oxo-2-alkenamides (**VII**) or cyclic derivatives thereof, 2,3-dihydro-3-imino-2-pyrrolones (**VIII**) [11] (Scheme 3).

We showed that pivaloylpyruvic acid (**IX**) [12, 13] in DMSO solution exists as an equilibrium mixture of two open-chain tautomers **IXx, IXy**, and a minor cyclic one **IXz**. Acid **IX** is a very reactive synthon that can be readily applied to introduction of a pivaloylpyrvoyl moiety into the molecules of NH-nucleophiles.

We studied in detail the reaction of acid **IX** with ammonia, primary and secondary amines. The reac-

Table 1. Yields, melting points, and elemental analyses of pivaloylpyruvamides **Va**–**f, k**–**m, o, p, r** and 2-imino derivatives thereof **Xa**–**i**

Compd. no.	Yield, %	mp, °C	Found, %			Formula	Calculated, %		
			C	H	N		C	H	N
Va	63	171–172[a]	56.36	7.43	8.31	$C_8H_{13}NO_3$	56.13	7.65	8.18
Vb	58	131–132	58.68	7.70	7.79	$C_9H_{15}NO_3$	58.36	8.16	7.56
Vc	52	173–174	62.24	9.17	6.41	$C_{11}H_{19}NO_3$	61.95	8.98	6.57
Vd	39	195–196	63.74	9.25	5.88	$C_{12}H_{21}NO_3$	63.41	9.31	6.16
Ve	92	120–121	63.29	9.47	6.33	$C_{12}H_{21}NO_3$	63.41	9.31	6.16
Vf	98	131–132	66.61	8.90	5.72	$C_{14}H_{23}NO_3$	66.37	9.15	5.53
Vk	48	150–151	63.12	6.50	4.74	$C_{16}H_{19}NO_5$	62.94	6.27	4.59
Vl	59	147–148	63.56	6.29	4.61	$C_{17}H_{21}NO_5$	63.94	6.63	4.39
Vm	74	122–123	59.53	8.15	5.62	$C_{12}H_{19}NO_4$	59.73	7.94	5.81
Vo	61	130–131	63.17	6.29	11.45	$C_{13}H_{16}N_2O_3$	62.89	6.50	11.28
Vp	53	104–105	62.76	6.61	11.37	$C_{13}H_{16}N_2O_3$	62.89	6.50	11.28
Vr	72	123–124	57.69	5.83	17.15	$C_{12}H_{15}N_3O_3$	57.82	6.07	16.86
Xa	71	121–123	75.11	7.73	8.20	$C_{22}H_{26}N_2O_2$	75.40	7.48	7.99
Xb	48	95–96	75.30	6.88	8.64	$C_{21}H_{24}N_2O_2$	74.97	7.19	8.33
Xc	56	109–110	75.63	7.72	8.16	$C_{22}H_{26}N_2O_2$	75.40	7.48	7.99
Xd	59	122–123	72.38	7.34	7.91	$C_{22}H_{26}N_2O_3$	72.11	7.15	7.64
Xe	61	120–121	71.86	7.12	7.45	$C_{22}H_{26}N_2O_3$	72.11	7.15	7.64
Xf	51	112–113	72.29	6.94	7.22	$C_{22}H_{26}N_2O_3$	72.11	7.15	7.64
Xg	53	130–131	70.68	6.74	13.23	$C_{19}H_{21}N_3O_2$	70.57	6.55	12.99
Xh	64	128–129	71.37	6.60	12.33	$C_{20}H_{23}N_3O_2$	71.19	6.87	12.45
Xi	69	130–131	68.20	6.32	12.19	$C_{20}H_{23}N_3O_3$	67.97	6.56	11.89

[a] mp 115°C [10].

tion occurs at room temperature in ethanol or tetrachloromethane and affords in fair yield the corresponding pivaloylpyruvamides **Va–r** (Scheme 4).

Yields, melting points, and elemental analyses of compounds **V** are listed in Table 1, and their spectral characteristics in Table 2. The constants of previously obtained amides **Vg–j, n, q** are given in [4].

The spectral characteristics of amides **V** are in sufficient agreement with the corresponding characteristics of the well known arylamides of the aroylpyruvic acids **I** [2, 4] that we have selected as model compounds.

In the IR spectra of compound **V** alongside the absorption band of the amide carbonyl appears a wide band at low frequencies corresponding to the stretching vibrations of the carbonyl groups in β-diketone moiety in the region 1560–1635 cm^{-1} indicating the presence of a chelate ring with an intramolecular hydrogen bond of the type –O–HO=CK [4].

Therewith in the ^1H NMR spectra of amides **V** recorded in DMSO-d_6 along with the singlet of the methine proton C^3H at 5.82–6.55 ppm frequently is observed a signal from protons of CH_2 group at 3.35–4.08 ppm (Table 2) evidencing that in the solution are present both keto-enol form **Vx** and minor β-diketone tautomer **Vy**. The content of the latter varies from 10 to 35%. In the ^1H NMR spectra of the model aroylpyruvamides **I** the marker signal of the methine proton C^3H is located in weaker field (about 0.7 ppm downfield, at 6.70–7.08 ppm) due to conjugation with the aryl moiety in 4 position of the chain.

The observed position of the proton signals from CH and CH_2 groups in compounds **V** is fairly consistent with the data of the prediction spectra for the model tautomeric structures **IVx** and **IVy** simulated with the use of the software from ACD/Labs Co (Scheme 5).

Since in the ^1H NMR spectra of amides **V** is lacking the characteristic signal of two coupled geminal protons of CH_2 group in the *4* position of cycle we can unambiguously conclude that no cyclic tauto-

Table 2. ^{1}H NMR spectra of pivaloylpyruvamides **Va, c, e, f, k, m, o, p** and 2-imino derivatives thereof **Xa–i**

Compd. no.	^{1}H NMR spectrum, δ, ppm (DMSO-d_6)
Va	1.05 s (9 H, Me_3C), 5.95 s (1H, CH)[a], 6.31 s (1H, OH), 7.15 s, 9.15 s (2H, NH_2)
Vc	1.22 br.s (15H, Me_3C + $\underline{Me}_2CH$), 4.08 br.s (1H, $CHMe_2$), 6.48 s (1H, CH)[a], 7.25 s (1H, OH), 8.12 br.s (1H, NH)
Ve	1.15 group of signals (15H, Me_3C + $2\underline{CH_3}CH_2$), 2.93 q (4H, 2 $CH_3\underline{CH_2}$), 3.85 s (2H, CH_2)[b], 5.92 s (1H, CH)[a]
Vf	1.08 s (9H, Me_3C), 3.81 br.s (11H, cyclohexyl), 6.55 s (1H, CH)[a]
Vk	1.05, 1.15 s (9H, Me_3C)[c], 3.35 s (2H, CH_2)[b], 3.90 s (3H, CH_3OCO), 6.10 s (1H, CH)[a], 6.70–8.05 m (4H, C_6H_4), 10.15, 12.15 br.s (1H, NH)[c]
Vl	1.15 s (9H, Me_3C), 3.52 br.s (8H, 4 CH_2 cycl.), 5.85 s (1H, CH)[a]
Vo	1.15 s (9H, Me_3C), 5.82 s (1H, CH)[a], 6.43–8.62 m (4H, 3-pyridyl), 11.68 br.s (1H, NH)
V®	1.15 s (9H, Me_3C), 4.08 s (2H, CH_2)[b], 6.18 s (1H, CH)[a], 6.82–8.88 m (4H, 4-pyridyl), 8.13 br.s (1H, NH)
Xa	1.05 s (9H, Me_3C), 3.98 br.s (2H, $Ph\underline{CH_2}NHC^2$, 4.48 br.s (2H, $Ph\underline{CH_2}NHCO$), 5.22 s (1H, CH)[a], 6.80–7.38 m (10H, 2 Ph), 10.88 br.s (1H, NHCO)
Xb	1.08 s (9H, Me_3C), 4.38 br.s (2H, $Ph\underline{CH_2}NHCO$), 5.52 s (1H, CH)[a], 6.58–7.15 m (10H, 2 Ph), 11.30 br.s (1H, NHCO)
Xc	1.08 s (9H, Me_3C), 2.18 s (3H, CH_3), 4.40 br.s (2H, $Ph\underline{CH_2}NHCO$), 5.54 s (1H, CH)[a], 6.50–7.28 m (9H, C_6H_5, C_6H_4), 12.05 br.s (1H, NHCO)
Xd	1.05 s (9H, Me_3C), 3.65 s (3H, CH_3O), 3.92 br.s (2H, $Ph\underline{CH_2}NHCO$), 5.05 s (1H, CH)[a], 6.70–7.40 m (9H, C_6H_5, C_6H_4), 12.35 br.s (1H, NHCO)
Xe	1.05, 1.17 s (9H, Me_3C)[c], 3.65, 3.75 s (3H, CH_3O)[c], 4.00 (2H, CH_2)[b], 4.55 br.s (2H, $Ph\underline{CH_2}NHC^2$, 5.45 s (1H, CH)[a], 6.55–7.45 m (9H, C_6H_5, C_6H_4), 10.70, 11.95 br.s (1H, NHCO)[c]
Xf	1.02 s (9H, Me_3C), 2.12 s (3H, CH_3), 3.67 s (3H, CH_3O), 5.58 s (1H, CH)[a], 6.55–7.25 m (8H, 2 C_6H_4), 11.82 br.s (1H, NHCO)
Xg	1.15 s (9H, Me_3C), 5.72 s (1H, CH)[a], 6.42–7.55 m (9H, C_6H_5, 2-pyridyl), 12.08 br.s (1H, NHCO)
Xh	1.15 s (9H, Me_3C), 2.15 s (3H, CH_3), 5.68 s (1H, CH)[a], 6.48–7.50 m (8H, C_6H_4, 2-pyridyl), 12.12 br.s (1H, NHCO)
Xi	1.05 s (9H, Me_3C), 3.62 s (3H, CH_3O), 5.45 s (1H, CH)[a], 6.00–7.75 m (8H, C_6H_4, 2-pyridyl), 11.95 br.s (1H, NHCO)

[a] Signal of the proton from methine group C^3H of tautomer **Vx** or respectively **Xx**.

[b] Signal of the proton from methylene group C^3H_2 of tautomer **Vy** or respectively **Xy**.

[c] Signals of protons from both forms **Vx** + **Vy** or respectively **Xx** + **Xy**.

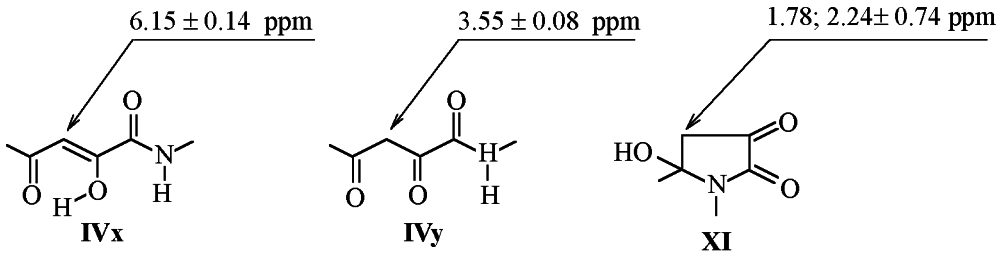
mer of the pyrrolidine-2,3-dione type is present similar to model structure **XI** (Scheme 5).

Amides **V** show the characteristic positive test (dark-red color) for enol hydroxy group with 10% alcoholic solution of iron(III) chloride.

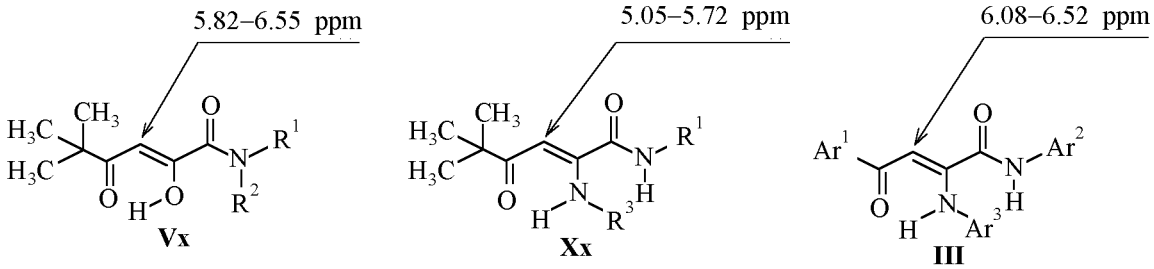
It is well known that the direct reaction of carboxylic acids with amines under mild conditions commonly results not in amides but in the corresponding ammonium salts [14]. The formerly studied reaction between aroylpyruvic acids with arylamines also did not result in amides **I** but in enamino derivatives at the α-carbonyl group, 4-aryl-2-arylamino-4-oxo-2-butenoic acids [15, 16]. However we established that the reaction of pivaloylpyruvic acid with ammonia and amines proceeds quite unusually : under mild conditions (at room temperature) and with no catalyst, and the reaction products are just the pivaloylpyruvamides **V**. This result is presumably due to involvement into the process of the equilibrium cyclic lactone form of the acid **IXz** with initial nucleophilic attack of amine at the lactone carbonyl followed by cycle opening and dehydration of the intermediate semiacetal (Scheme 4). Thus we developed a method of unusual acylation of amines with a carboxylic acid capable to react in an equilibrium lactone form.

Pivaloylpyruvamides **Vg, j, n** readily react at room temperature in ethanol with benzylamine, aniline, *p*-toluidine or *p*-anisidine yielding substitution products at the α-carbonyl group, the cor-

Scheme 5.



Scheme 6.

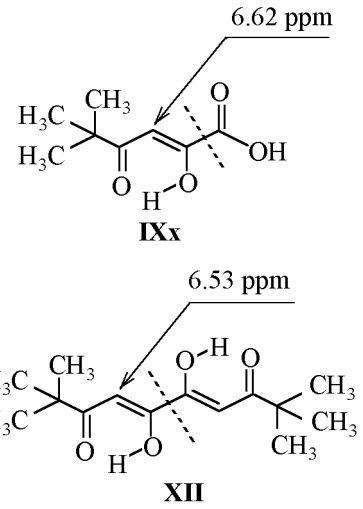


responding amides of (*Z*)-2-benzylamino- or 2-arylamino-5,5-dimethyl-4-oxo-2-hexenoic acid (**Xa–i**) (Scheme 4). The physical constants and elemental analyses of compounds **X** are presented in Table 1, and their spectral characteristics in Table 2. The spectral data of amides **X** are consistent with those of model arylamides of 4-aryl-2-arylamino-4-oxo-2-butenoic acid [5] and of the initial compounds **V**.

In the ^{1}H NMR spectra of compounds **X** registered in DMSO-d_6 the methine proton signal C^3H appears at 5.05–5.72 ppm, i.e., upfield from the corresponding signals of the original amides **Vx** on the average by 0.8 ppm (Table 2) due to the substitution of the hydroxy group of the enol with amino group of the enamine (Scheme 6). Yet the replacement of the *tert*-butyl substituent by aryl fragment in C^4 position and going from compounds **Xx** to amides **III** results in the downfield shift of the marker proton on the average by 0.9 ppm. Note that the positions of the proton signals from C^3H of the compared compounds **Vx** and **III** are nearly the same.

In the ^{1}H NMR spectrum of amide **Xe** we observed both the singlet from methine proton C^3H at 5.45 ppm and the signal of two protons of the CH_2 group at 4.00 ppm alongside the double set of signals from the other proton-containing groups (Table 2). This fact evidences the presence of both keto-enol **Xx** and β-diketone **Xy** tautomers; the content of the latter amounts to 25%.

Scheme 7.



The formation of compounds **X** results from a nucleophilic attack of amine on the C^2 atom in the initial amides **Va** in fair agreement with the known data on the reaction mechanism of aroylpyruvamides **I** with aniline [17], and also with the new findings on the orbital control of the reactions between nucleophiles and aroylpyruvic acids and their derivatives [18, 19].

It should be also noted that in the ^{1}H NMR spectrum of the initial pivaloylpyruvic acid recorded in DMSO-d_6 we observed 3 equilibrium forms: **IXx** (71%), **IXy** (24%), and **Xz** (5%). This spectral character does not contradict previously obtained data

on the presence of a number of prototropic forms in the solutions of aroylpyruvic acids [19–22]. These data to a certain extent also are consistent with the presence of several open-chain and cyclic forms in solutions of substituted tetraketones containing two linked β-dicarbonyl fragments [23–25]. The ^{1}H NMR spectrum of acid **IXx** is in good agreement also with the spectral characteristics of the open-chain dienol form of the similar in structure 2,2,9,9-tetramethyl-3,5,6,8-tetraoxodecane (**XII**) [23] (Scheme 7).

The synthesized amides **V** and **X** show bacteriostatic activity toward *Staphyloccus Aurous* and *Escherichia Coli* with a minimum inhibiting concentration from 125 to 1000 μg ml^{-1}.

In ten pivaloylpyruvamides **Ve–h, k, l–q** was found a pronounced analgetic activity: the time of defensive reflex in tests on mice shown by these compounds is from 18.6 to 27 s. The effect of compounds **V** is comparable with the analgetic effect of aroylpyruvamides **I** [4, 19, 26].

EXPERIMENTAL

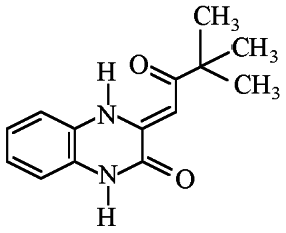
IR spectra of compounds **V, IX, X** were recorded on spectrometers UR-20 and Specord M-80 from mulls in mineral oil. ^{1}H NMR spectra were registered on spectrometers RYa-2310 (60 MHz) and Bruker AC-300 (300.13 MHz) in DMSO-d_6 and $CDCl_3$, internal reference TMS or HMDS. Mass spectra were measured on MS-30 instrument (Kratos) in direct input mode, emission current 1000 mA, ionizing voltage 70 eV, evaporator temperature 100°C. The routine used in simulation of the NMR spectra was received from ACD/Labs Software, Toronto, Canada (http://www.acdlabs.com). The individuality of compounds was tested by TLC on Silufol UV-254 plates in a system benzene–ether–acetone, 10 : 9 : 1, development in iodine vapor. The physical constants of amides **V g–j, n, q** are published in [4]. According to the literature data the initial reagent, pivaloylpyruvic acid (**IX**), can be prepared by basic hydrolysis of its ethyl ester [12]; also exists a short communication without preparative details on synthesis of acid **IX** by Claisen condensation [13].

Pivaloylpyruvamides Va–r. To a solution of 1.35 g (7.8 mmol) of pivaloylpyruvic acid (**IX**) in 20 ml of ethanol was added 2 ml of 25% aqueous ammonia or 20% water solution of methylamine (in the synthesis of compounds **Va** or **Vb**), or to a solution of 1.35 g (7.8 mmol) of initial acid (**IX**) in 20–30 ml of ethanol or tetrachloromethane was added at stirring a solution of 7.8 mmol of the appropriate amine in 15–20 ml of ethanol or tetrachloromethane. The mixture was left standing at room temperature for 24 h. The separated precipitate was filtered off and recrystallized from ethanol, dioxane, from toluene–hexane mixture (2 : 1), or tetrachloromethane.

Benzylamide of pivaloylpyruvic acid (Vg) [4]. IR spectrum (ν, cm^{-1}): 3284 (CONH), 1665 (CONH), 1610–1540 (CO chelate).

Pivaloylpyruvic acid (IX). To 100 ml of methanol preliminary distilled on sodium metal was added by portions 9.2 g (0.4 g-atom) of sodium, then methanol was distilled off, and to the dry sodium methylate was added 150 ml of anhydrous ethyl ether. At cooling to the suspension was added dropwise while stirring a mixture of 29.2 g (0.2 mol) of diethyl oxalate and 40 g (0.4 mol) of pinacolin. On the next day to the precipitate of the sodium enolate was added at stirring 40 ml of hot water and by portions concn. HCl till pH 3–4. The solution was evaporated, and the dry residue was recrystallized from tetrachloromethane or from a mixture toluene–hexane (1 : 1). We obtained colorless needle-like crystals of acid **IX**. Yield 24.6 g (71%), mp 54–55°C (publ.: 64°C [12]). IR spectrum (ν, cm^{-1}): 3455–3510 (COOH), 1708–1675 (COOH), 1622– 1615, 1590–1580 (C=O chelate), 1458, 1372, 1293, 1257, 1138, 1115. ^{1}H NMR spectrum ($CDCl_3$, δ, ppm): 1.20 s (9H, $3CH_3$), 6.62 s (1H, CH): 100% enol form (IXx). ^{1}H NMR spectrum (DMSO-d_6, δ, ppm): 1.02 s [9H, $3CH_3$, form (**IXz**), 5%], 1.08 s [9H, $3CH_3$, form (**IXy**), 24%], 1.17 s [9H, $3CH_3$, form (**IXx**), 71%], 2.90, 3.38 two d [2H, CH_2, form (**IXz**)], 4.06 s [1H, CH_2, form (**IXy**)], 5.42 s [1H, OH, form (**IXz**)], 6.50 s [1H, CH, form (**IXx**)], 13.90–14.30 br.s [2H, 2OH in COOH, forms (**IXx**) and (**IXy**)]. Found, %: C 56.24; H 6.73. $C_8H_{12}O_4$. Calculated, %: C 55.81; H 7.02.

From the filtrate after crystallization was isolated 1.3 g (2%) of 5,6-dihydroxy-2,2,9,9-tetramethyl-4,6-decadiene-3,8-dione (**XII**), mp 85–86°C (from ethanol) (publ.: 98°C [27]. IR spectrum (ν, cm^{-1}): 1605, 1580–1545 (C=O chelate), 1530, 1458. ^{1}H NMR spectra (in $CDCl_3$ and DMSO-d_6) were published in [23]. The insoluble residue after crystallization was presumably an uncommonly inert against oxygen sodium salt of the enol form of acid **IXx** that we did not succeed to convert into acid **IX** even in strongly acidic medium (H_2SO_4). ^{1}H NMR spectrum of the salt (DMSO-d_6, δ, ppm): 1.05 s (9H, $3CH_3$), 5.91 s (1H, CH). The structure of the salt is indirectly supported by its conversion into 3-pivaloylmethylene-3,4-dihydro-1*H*-2-quinoxalone (**XIII**) [15] when treated with *o*-phenylenediamine. The analogous reaction occurs with pivaloylpyruvic acid (**IX**).

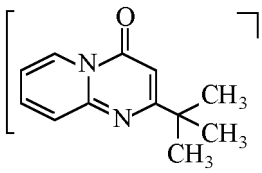
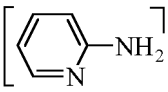


XIII

Amides of (*Z*)-2-benzylamino- and 2-arylamino-5,5-dimethyl-4-oxo-2-hexenoic acid Xa–i. To a solution of 1.6 mmol of an appropriate amide **Vg, j, n** in 20–30 ml of ethanol was added at stirring a solution in 10–15 ml of ethanol of 1.6 mmol of benzylamine, aniline, *p*-toluidine or *p*-anisidine. The mixture was left standing at room temperature for 24 h. The separated precipitate was filtered off and recrystallized from toluene.

Benzylamide of (*Z*)-2-(*p*-methoxyphenylamino)-5,5-dimethyl-4-oxo-2-hexenoic acid Xd. IR spectrum (ν, cm^{-1}), 3200 (CONH), 1670 (CONH), 1612–1588 (CO chelate).

***p*-Methoxyphenylamide of (*Z*)-2-(*p*-tolylamino)-5,5-dimethyl-4-oxo-2-hexenoic acid Xf.** Mass spectrum, *m/z* (I_{rel}, %), molecular ion peak absent, fragment ion peaks of I_{rel} > 5%: 233 (23) $[M-4\text{-}CH_3OC_6H_4\cdot C{\equiv}N]^+$, 217 (7) $[M-4\text{-}CH_3OC_6H_4N{=}C{=}O]^+$ or $[(CH_3)_3CCOCH{=}CHNHC_6H_4CH_3\text{-}4]^+$, 177 (9), 176 (100) $[M-4\text{-}CH_3C_6H_4\text{-}(CH_3)_3CCOCH_2]^+$ or $[4\text{-}CH_3OC_6H_4NHCOC{\equiv}N]^+$, 174 (13), 161 (19), 160 (42) $[M-4\text{-}CH_3OC_6H_4\text{-}(CH_3)_3CCOCH_2]^+$, 158 (6), 134 (5), 133 (32) $[4\text{-}CH_3OC_6H_4C{\equiv}N]^+$, 132 (7), 117 (7) $[4\text{-}CH_3C_6H_4C{\equiv}N]^+$, 105 (5), 104 (9), 91 (8) $[4\text{-}CH_3C_6H_4]^+$, 80 (6), 79 (6), 77 (12) $[C_6H_5]^+$, 65 (8), 64 (6), 63 (8), 57 (19) $[(CH_3)_2CHCH_2]^+$, 53 (8), 52 (9), 51 (7).

2-Pyridylamide of (*Z*)-2-(*p*-methoxyphenylamino)-5,5-dimethyl-4-oxo-2-hexenoic acid Xi. Mass spectrum, *m/z* (I_{rel}, %), molecular ion peak absent, fragment ion peaks of I_{rel} > 5%: 277 (18) $[M-(CH_3)_3C\text{-}H_2O\text{-}H]^+$, 220 (12) $[M-4\text{-}CH_3OC_6H_4\cdot C{\equiv}N]^+$, 202 (18)  , 176 (15), 175 (10), 174 (100) $[M-(CH_3)_3C\text{-}4\text{-}CH_3OC_6H_4NH]^+$, 147 (8), 146 (9), 133 (9) $[4\text{-}CH_3OC_6H_4C{\equiv}N]^+$, 132 (9), 120 (6), 108 (6), 105 (9), 104 (8), 94 (22)  , 92 (10), 91 (11), 78 (13), 77 (20) $[C_6H_5]^+$, 76 (8), 67 (21), 66 (8), 65 (11), 64 (10), 57 (31) $[(CH_3)_2CHCH_2]^+$, 53 (8), 52 (17), 51 (10).

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