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# Acylpyruvic Acid Amides and Hydrazides: XII.[1] Reaction of 4-Aryl-2-hydroxy-4-oxo-2-butenic Acids Arylamides with Triphenylphosphoranylideneacetic Acid Esters

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**Abstract** — 4-Aryl-2-hydroxy-4-oxo-2-butenic (aroylpyruvic) acid arylamides react with triphenylphosphoranylidenacetic acid esters to form products of Wittig reaction at α-carbonyl group, the 5-aryl-3-arylaminocarbonyl-5-oxo-3-pentenoic acid esters. Features in structure of the obtained compounds are discussed.
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The Wittig reaction of aliphatic, alicyclic and aromatic α-dicarbonyl compounds (including α-ketoesters) with methylenephosphoranes leads to formation of the products of mono- and bis-olefination, depending on the reagent ratio and reactivity [2–8].

Among β-dicarbonyl compound, were studied reactions of acetoacetic and benzoylacetic esters with acetyl- and benzoylmethylenetriphenylphosphoranes, and were isolated the products of C-acylation of the latter compounds with successive heterocyclization, 2,6-disubstituted 4*H*-pyran-4-ones and 4-acylmethylene-4*H*-pyrans [9, 10]. Features in the selective olefination of the carbonyl group in five- and six-membered dioxo heterocycles with phosphoric ylides and competitive acylation of the ylides has been considered in [7, 11–16]. Reactions of acyclic polycarbonyl systems containing α- and β-dicarbonyl fragments simultaneously, including acylpyruvic acids and related esters or amides were not studied before our investigations.

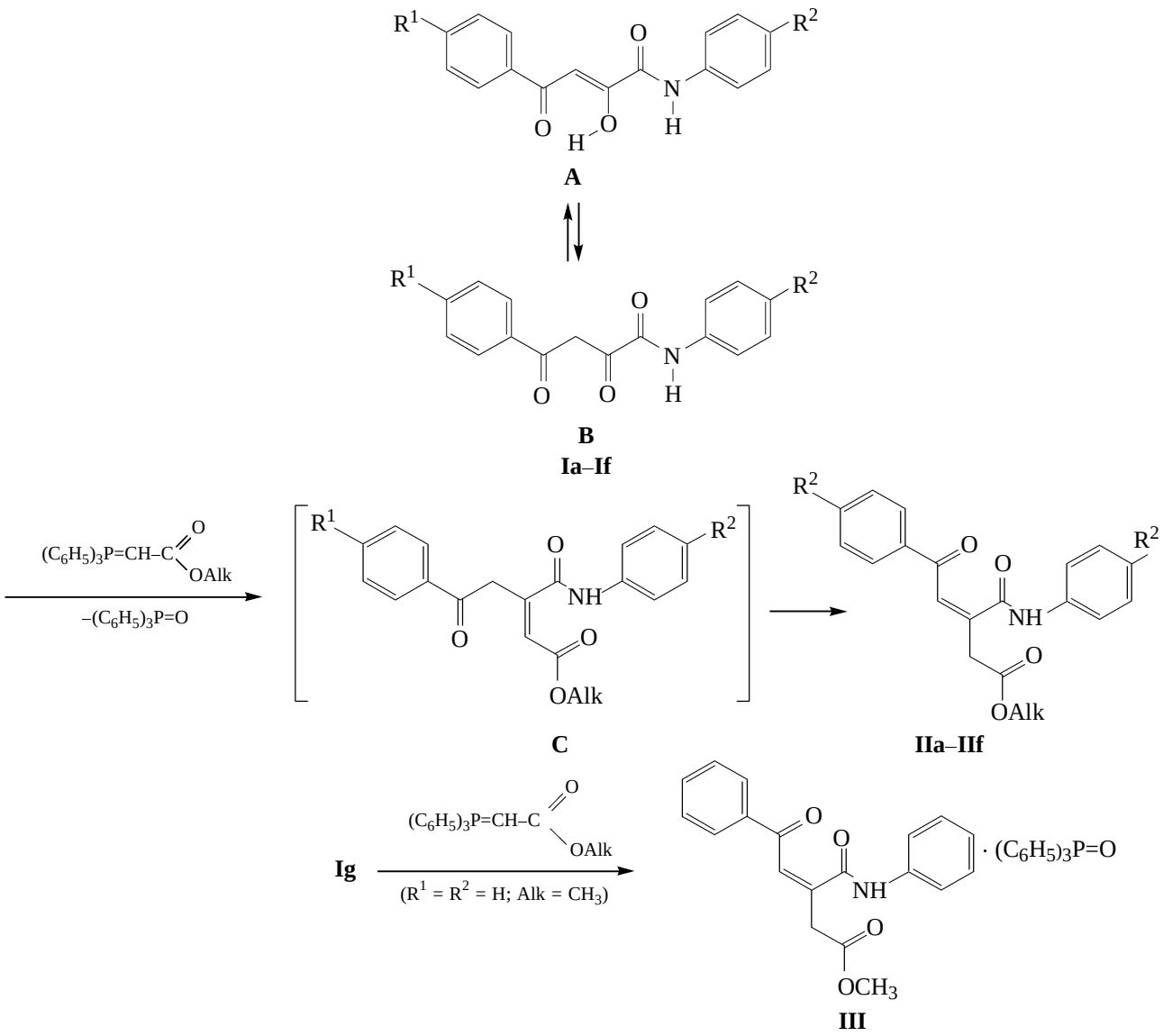
We established that 4-aryl-2-hydroxy-4-oxo-2(*Z*)-butenic (aroylpyruvic) acid arylamides (**Ia**–**If**) [their solutions contain both enol **A** and β-diketonate tautomeric forms **C**] readily react with triphenylphosphoranylideneacetic acid esters forming Wittig's olefination products at α-carbonyl group, the 5-aryl-3-arylaminocarbonyl-5-oxo-3(*Z*)-pentenoic acid esters (**IIa**–**IIf**) (for preliminary publication see [18]) and triphenylphosphine oxide (Scheme 1).

In the reaction of 2-hydroxy-4-oxo-4-phenyl-2-butenic acid phenylamide (**Ig**) with methyl triphenylphosphoranylideneacetate we isolated methyl 5-oxo-5-phenyl-3-phenylaminocarbonyl-3(*Z*)-pentenoate adduct with triphenylphosphine oxide (**III**) of 1 : 1 composition (Scheme 1). We failed to separate components of the complex **III** by ordinary methods. Formation of such adduct is not unexpected: the stable complexes of triphenylphosphine oxide with carbonyl compound are well known (e.g., see [18]).

Compounds **IIa**–**IIf** and **III** obtained in preparative yields are yellowish crystalline substances insoluble in water and hexane, poorly soluble in diethyl ether and soluble in most other ordinary organic solvemts including ethanol, acetone, acetonitrile and chloroform. Structure of the synthesized compounds **IIa**–**IIf** and adduct **III** is confirmed by the methods of UF, IR and $^1$H NMR spectroscopy and by mass spectrometry. IR spectra of compounds **IIa**–**IIf** include the bands of stretching vibration at relatively high frequency 1744–1753 cm$^{-1}$ related to carbonyl group in the esters. Its position points to the absence of unsaturated group at $C^2$ [19] of the assumed intermediate **C** in the Wittig reaction (Scheme 1). Note for comparison that in the spectra of unsaturated 1,4-dicarboxylic acid ester arylamides **IV** (Scheme 2) comprising the considered functional part of structure **C** the ester carbonyl frequency is no over than 1710 cm$^{-1}$ [20]. Occurrence in the IR spectra of compounds **IIa**–**IIf** of the strong bands at 3338–3390 and 1672–1692 cm$^{-1}$ NH and CO of amide carbonyl stretching vibrations also well conforms to their structure.

[1] For communication XI, see [1].

**Scheme 1.**



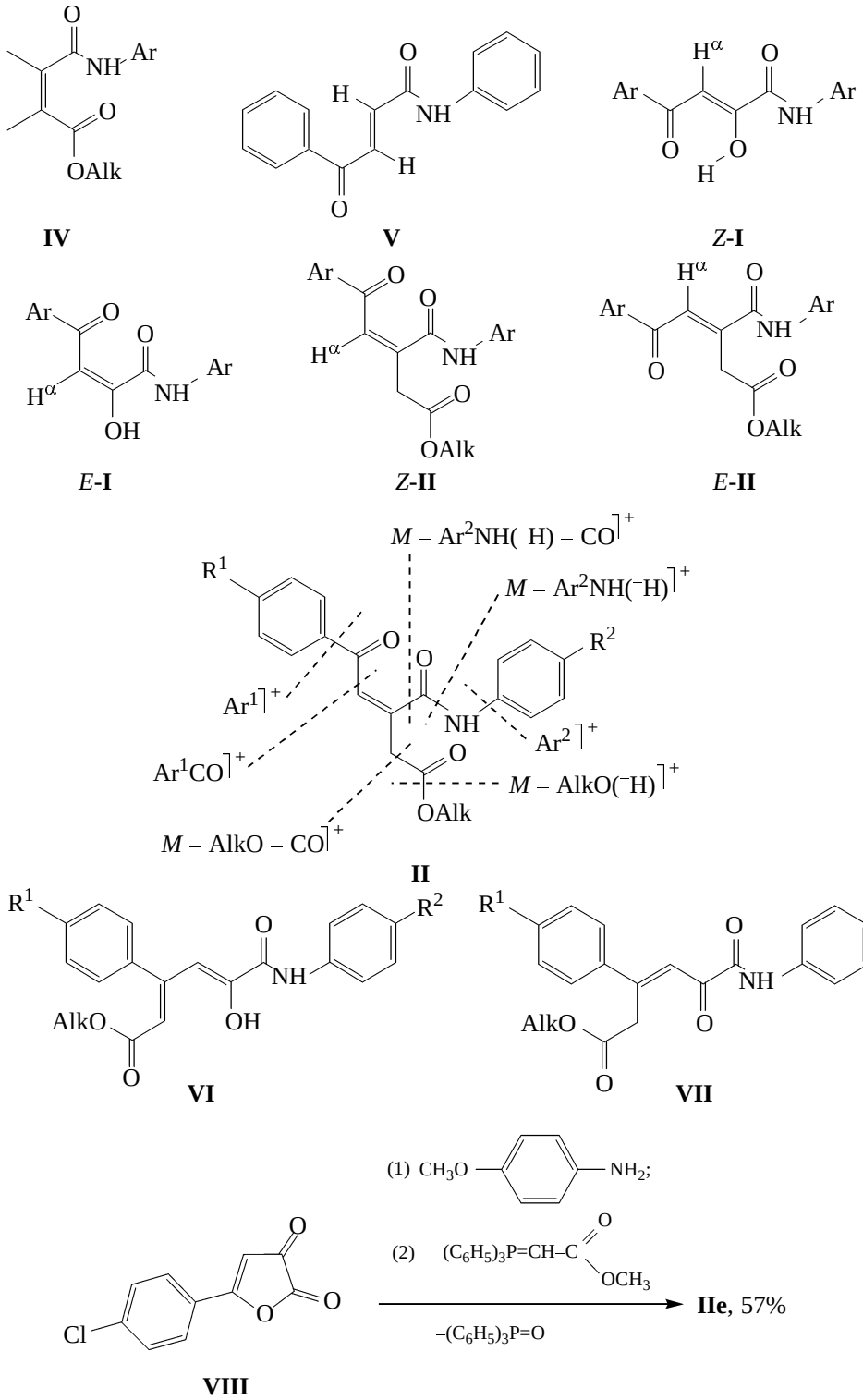

Alk = $CH_3$; $R^1$ = H, $R^2$ = $CH_3$ (**Ia, IIa**), $CH_3O$ (**Ib, IIb**); $R^1$ = $CH_3$, $R^2$ = $CH_3O$ (**Ic, IIc**), Br (**Id, IId**); $R^1$ = Cl, $R^2$ = $CH_3O$ (**Ie, IIe**); $R^1$ = $R^2$ = H (**Ig**); Alk = $C_2H_5$; $R^1$ = Br, $R^2$ = $CH_3$ (**If, IIf**).

UV spectra of compounds **IIa**–**IIf** and **III** contain bands $\lambda_{max}$ 225–232 nm ($\log\varepsilon$ 4.17–4.32) and 313–331 nm ($\log\varepsilon$ 3.34–3.66). Position of the long-wave band is close to the maximum absorption of benzoylacrylic phenylamide **V** $\lambda_{max}$ 310 nm [21], which has chromophore system related to that of compounds **II** (Scheme 2). The isomeric to **II** compounds with structure **C** would contain shorter chromophore system. In the spectra of taken for comparison arylamides **IV** with double bond fixed in α-position the long-wave maximum exerts hypsochromic shift ($\lambda_{max}$ 295 nm or lower) [20] as compared to the β-unsaturated esters **II**.

Note for comparison that in the UV spectra of amides **I** the long-wave maximum occurs at higher wavelength, $\lambda_{max}$ 340–345 nm ($\log\varepsilon$ ~4.40) [22], than that of compounds **II**, due to somewhat longer cheomophore system of 2(*Z*)-enol form (**A**) of the parent amides **I** due to intermolecular H-bond of $C^2$–OH···O=$C^4$ type in the six-membered OH-chelate ring of the β-dicarbonyl group in **A** structure [22].

The $^1$H NMR spectra of compounds **IIa**–**IIf** and **III** besides the common signals of alkoxy groups of the ester moiety, protons 2 of two benzene rings and

**Scheme 2.**




Alk = $CH_3$, $C_2H_5$; $R^1$ = H, $CH_3$, Br, Cl; $R^2$ = H, $CH_3$, $CH_3O$, Br.

amide group NH, occurs the singlets of two protons in the $C^2H_2$ group (δ 3.25– 3.54 ppm) and $C^4H$ methyne proton in aroylmethylene fragment at δ 4.77–5.20 ppm (in deuterochloroform), δ 6.31–6.88 ppm (in acetone-$d_6$) and δ 6.92, 6.94 ppm (in DMSO-$d_6$: two compounds as an example). In polar media the signal

Comparison of experimental and calculated values of chemical shift of methyne protons $\delta_{H^\alpha}^{E(Z)}$ in $^1$H NMR spectra (δ, ppm) of compounds **I** and **II**

| Comp. no. | Solvent | $\delta_{H^\alpha}^{exp}$ | $\delta_{H^\alpha}^{calc}$ | | $\Delta\delta_{H^\alpha} = \lvert\delta_{H^\alpha}^{exp} - \delta_{H^\alpha}^{calc}\rvert$ | |
|---|---|---|---|---|---|---|
| | | | *Z* isomer | *E* isomer | *Z* isomer | *E* isomer |
| **Ia**–**If** | $CDCl_3$ | 6.82–7.10 | | | 0.74–1.02 | 1.16–1.44 |
| **I** | DMSO-$d_6$ [a] | 6.75–7.20 | 6.08 [b] | 5.66 | 0.43–1.12 | 0.85–1.54 |
| **IIa**–**IIf** | $CDCl_3$ | 4.77–5.20 | | | 1.41–1.84 | 2.07–2.50 |
| **IIa**–**IIf** | Acetone-$d_6$ | 6.31–6.51 | 6.61 | 7.27 | 0.10–0.30 | 0.76–0.96 |

[a] Published data [24]. [b] Calculation without consideration of intramolecular H-bond in OH-chelate ring.

of methyne proton is shifted downfield by δ 1.6 ppm (in deuteroacetone) and δ 1.9 ppm (in DMSO-$d_6$). The shift is probably induced by solvating polarization of carbonyl group in the $C^5(=O)$–$C^4H$ fragment, as we also noted earlier for the related structures with the double bond activated by carbonyl acceptors [15, 23].

In the solutions of parent aroylpyruvic amides **I** predominates enol structure **A**: 4-aryl-2-hydroxy-4-oxo-2(*Z*)-butenic acid arylamide, while β-diketone tautomer **B** is a minor component [24] (Scheme 1). The enol form 2*Z*-**A** is stabilized by intramolecular H-bond of OH-chelate type [22], *E*-isomer in the case of amides **I** was not detected. For elucidation of steric position of the substituents at the ethylene fragment $C^3=C^4H^\alpha$ in the target compounds **IIa**–**IIf** in comparison with the known orientation of substituents at the unsaturated fragment $C^2=C^3H^\alpha$ of the parent amides **Ia**–**Ig** (Scheme 2) we calculated expected chemical shift of the methine proton in the $^1$H NMR spectra of these compounds by additive scheme taking shielding parameters of substituents at their different orientation near $H^\alpha$ protin [19].

*For amides* **I**:

$$\delta_{H^\alpha}^{E(Z)} = \delta_{C=C}^{0} + \delta_{OH}^{E(Z)} + \delta_{CONHAr}^{E(Z)} + \delta_{COAr}^{gem},$$

*For esters* **II**:

$$\delta_{H^\alpha}^{E(Z)} = \delta_{C=C}^{0} + \delta_{OH}^{E(Z)} + \delta_{CH-COOAlk}^{E(Z)} + \delta_{COAr}^{gem}.$$

Here $\delta_{H^\alpha}^{E(Z)}$ is calculated chemical shift of methyne $H^\alpha$ proton in *E* and *Z* isomers of compounds **I** and **II**, $\delta_{C=C}^{0}$ is chemical shift of methyne $H^\alpha$ in CH= group of ethylene taken as origin (5.28 ppm [19]); $\delta_{OH}^{E(Z)}$, $\delta_{CH-COOAlk}^{E(Z)}$, $\delta_{CONHAr}^{E(Z)}$, and $\delta_{COAr}^{gem}$ are shielding parameters of substituents in olefins (tabulated values).

Comparison of experimental and calculated values of methine proton chemical shifts $\delta_{H^\alpha}^{E(Z)}$ (see table) shows that these parameters match better to *Z* isomers of compounds **II**: $\Delta\delta_{H^\alpha} = \lvert\delta_{H^\alpha}^{exp} - \delta_{H^\alpha}^{calc}\rvert$ for the *Z* isomers is 0.10–0.30 ppm (in acetone-$d_6$) and 1.41–1.84 ppm (in deuterochloroform), while for *E* isomers respectively 0.76–0.96 and 2.07–2.50 ppm. Thus, the calculation attests in favor of *Z* configuration of esters **II**. As to the objects of comparison **I** (see table), calculation also leads to conclusion of preference of the *Z* isomers, in conformity with the established earlier for the amides **I** [22, 24]. These data confirm also reliability of such a calculation for structural analysis of organic compounds (see [14, 15]).

Mass spectra of compounds **II** show characteristic peaks of fragmental ions corresponding to the principal directions of fragmentation under electron impact (Scheme 2). Presence in the spectra of esters **II** of the strong peaks corresponding to aroyl ions (4-$R^1C_6H_4$–C=O) allow to reject alternative structures **VI** and **VII** and their geometric isomers for these compounds and confirms proceeding of the Wittig reaction at the carbonyl group $C^2=O$ of the aroylpyruvic acids **I**.

Noteworthy that compounds **II** give strong red color with 10% solution of NaOH in alcohol and their solutions in trifluoroacetic acid are red-brown in color. These tests allow to perform qualitative detection of compounds **I** and monitoring their reactions.

Reaction of aroylpyruvic arylamides **I** with triphenylphosphoraylideneacetic esters proceeds in correspondence with the mechanism of Wittig reaction [7, 25] with substitution of oxygen atom in the a α-ketogroup of the diketon form **B** of arylamides by alcoxycarbonylmethylene fragment leading to formation of compounds **II** via isomeric intermediate **C** with $C^2 \rightarrow C^3$ migration of double bond. The fact of proceeding of the competitive olefination reaction at the α-ketone carbonyl confirms the data on higher electrophilicity of the carbon aton in α-ketogroup than in the γ-carbonyl group of the parent amides **I** [22, 24].

As is known, the synthesis of the parent aroylpyruvic amides **I** is conducted under mild conditions

with quantitative yield at the reaction of available 5-arylfuran-2,3-diones with aromatic amines [22, 24]. In the three-component reaction of 5-(4-chlorophenyl)-furan-2,3-dione (**VIII**) with *p*-anisidine and methyl triphenylphosphoraylideneacetate without isolation of intermediately formed amide **Ie** we prepared methyl 3-(4-methoxyphenyl)aminocarbonyl-5-oxo-5-(4-chlorophenyl)-3(*Z*)-pentenoate (**IIe**) in 57% yield and triphenylphosphine oxide (Scheme 2). Thus, compounds **II** can be readily obtained by Wittig reaction from aroylpyruvic amides and directly from furan-2,3-diones as well.

Compounds **IIa**–**IIf** possess marked antimicrobial activity to reference strains of *Staphylococcus aureus* P-209 and *Escherichia coli* M17 [17].

In attempted reaction of free aroylpyruvic acids or methyl esters with acylmethylenetriphenylphosphoranes we failed to isolate individual compounds due to strong tarring.

## EXPERIMENTAL

IR spectra of esters **II** and adduct **III** were recorded on UR-20 and Specord M-80 spectrometers from the pasts with Vaseline oil. UV spectra of compounds **II** and **III** were recorded on a Specord UV-Vis spectrophotometer from solutions in ethanol $10^{-4}$–$10^{-5}$ M. $^1$H NMR spectra of compounds **II** and **III** and of the reference substances **I** were registered on RYa-2310 (60 MHz) and Bruker DRX-500 (500 MHz) instruments with the solvents deuterochloroform, acetone-$d_6$ and DMSO-$d_6$, and internal references HMDS or TMS. Mass spectra of compounds **II** were taken on a Varian MAT-311 instrument with direct inlet mode (electron impact), emission current 1000 mA, ionizing voltage 70 eV, evaporator temperature 120–150°C.

TLC on Silufol UV-254 was used for monitoring reactions and confirming individuality of the products obtained, the system was benzene–diethyl ether–acetone 10 : 9 : 1, development with iodine vapor.

Parent aroylpyruvic amides **I** were prepared from 5-arylfuran-2,3-diones by ring cleavage at the action of arylamines [22, 24, 26, 27]. Below are given earlier not published data on the $^1$H NMR spectra of compounds **Ia**, **If**, and **Ig**. 5-(4-Chlorophenyl)furan-2,3-dione (**VIII**) was prepared by dehydration of 2-hydroxy-4-oxo-4-(4-chlorophenyl)-2(*Z*)-butenic acid at the action of acetic anhydride [28]. Triphenylphosphoraylideneacetic acid esters were synthesized alongside the published method [29].

**Esters of 5-aryl-3-arylaminocarbonyl-5-oxo-3(*Z*)-pentenoic acid (IIa–IIf) and adduct of methyl 5-oxo-5-phenyl-3-phenylaminocarbonyl-3(*Z*)-pentenoate with triphenylphosphine oxide (III)** *(general procedure). a.* A mixture of equimolar amounts (5 mmol each) of corresponding aroylpyruvic arylamides **Ia**–**Ig** and esters of triphenylphosphoraylideneacetic acid was heated with stirring in 50–70 ml of ethyl acetate to complete dissolving and then refluxed for 0.5–1 h. Solvent was then evaporated and residue was grinded with ether and recrystallized from ethanol or acetonitrile. Compounds **IIa**–**IIf** and **III** were obtained. From the residue after isolation of a compound **II** was isolated triphenylphosphine oxide, yields 52–74%, mp 156–157°C (from tetrachloromethane).

**Methyl 3-(4-methylphenyl)aminocarbonyl-5-oxo-5-phenyl-3(*Z*)-pentenoate (IIa).** Yield 1.50 g (89%), mp 127–128°C (from ethanol). IR spectrum, ν, $cm^{-1}$: 3340 (CO*NH* amide), 1748 ($C^1$=O ester), 1675–1683 (*CO*NH amide, $C_6H_5COCH$=). UV spectrum, $\lambda_{max}$ (log ε), nm: 225 (4.26), 331 (3.66). $^1$H NMR spectra, acetone-$d_6$, δ, ppm: 2.12 s (3H, $CH_3$), 3.30 s (2H, $C^2H_2$), 3.59 s (3H, $OCH_3$ in $COOCH_3$), 6.51 s (1H, $C^4H$), 7.00–7.65 m (9H, $C_6H_5$, $C_6H_4$), 7.44 s (1H, NH). Found, %: C 71.47; H 5.42; N 3.90. $C_{20}H_{19}NO_4$. *M* 337.37. Calculated, %: C 71.20; H 5.68; N 4.15.

**Methyl 3-(4-methoxyphenyl)aminocarbonyl-5-oxo-5-phenyl-3(*Z*)-pentenoate (IIb).** Yield 1.50 g (85%), mp 151–152°C (from ethanol). IR spectrum, ν, $cm^{-1}$: 3390 (CO*NH* amide), 1745 ($C^1$=O ester), 1692–1680 (*CO*NH amide, $C_6H_5COCH$=). UV spectrum, $\lambda_{max}$ (log ε), nm: 230 (4.32), 327 (3.58). $^1$H NMR spectrum, $CDCl_3$, δ, ppm: 3.54 s (2H, $C^2H_2$), 3.65 s (3H, $CH_3O$ in 4-$CH_3OC_6H_4$), 3.69 s (3H, $OCH_3$ in $COOCH_3$), 4.88 s (1H, $C^4H$), 6.52–7.40 m (9H, $C_6H_5$, $C_6H_4$), 7.24 s (1H, NH). Found, %: C 67.77; H 5.60; N 3.84. $C_{20}H_{19}NO_5$. *M* 353.37. Calculated, %: C 67.98; H 5.42; N 3.96.

**Methyl 3-(4-methoxyphenyl)aminocarbonyl-5-oxo-5-(4-methylphenyl)-3(*Z*)-pentenoate (IIc).** Yield 1.40 g (76%), mp 143–144°C (from ethanol). IR spectrum, ν, $cm^{-1}$: 3355 (CO*NH* amide), 1748 ($C^1$=O ester), 1675–1685 (*CO*NH amide, 4-$CH_3C_6H_4$·COCH=). UV spectrum, $\lambda_{max}$ (log ε), nm: 227 (4.25), 320 (3.45). $^1$H NMR spectra, $CDCl_3$, δ, ppm: 2.22 s (3H, $CH_3$), 3.32 s (2H, $C^2H_2$), 3.62 s (3H, $CH_3O$ in 4-$CH_3OC_6H_4$), 3.67 s (3H, $OCH_3$ in $COOCH_3$), 5.20 s (1H, $C^4H$), 6.62–7.40 m (8H, $2C_6H_4$), 7.18 s (1H, NH). Mass spectrum, *m/z* ($I_{rel}$, %), the ions with $I_{rel}$ > 5% are listed: 245 (6) $[M - 4\text{-}CH_3OC_6H_4NH]^+$, 244 (37) $[M - 4\text{-}CH_3OC_6H_4NH - H]^+$, 217 (7) $[M - 4\text{-}CH_3OC_6H_4NH - CO]^+$, 216 (40) $[M - 4\text{-}CH_3O\cdot C_6H_4NH - CO - H]^+$ or $[4\text{-}CH_3C_6H_4CO–CH=C=CH–$

$COOCH_3]^+$, 213 (10) [*M* – 4-$CH_3OC_6H_4NH$ – $OCH_3$ – H]$^+$ or [4-$CH_3C_6H_4CO$–CH=C(C–O)–CH=C=O]$^+$, 186 (8) $[C_{12}H_{10}O_2]^+$, 185 (12) [*M* – 4-$CH_3OC_6H_4NH$ – CO – OCH3 – H]$^+$ or $[C_{12}H_9O_2]^+$, 157 (7) $[C_{11}H_9O]^+$, 129 (7), 124 (7), 123 (77) [4-$CH_3OC_6H_4NH_2]^+$, 119 (36) [4-$CH_3C_6H_4C$–O]$^+$, 109 (8), 108 (100) [4-$CH_3$·$OC_6H_5]^+$, 91 (22) [4-$CH_3C_6H_4]^+$, 80 (31), 65 (14), 63 (5), 53 (12), 52 (8). Found, %: C 61.47; H 4.30; N 9.23. $C_{16}H_{14}N_2O_5$. *M* 314.29. Calculated, %: C 61.14; H 4.49; N 8.91. Found, %: C 68.87; H 5.64; N 3.96. $C_{21}H_{21}NO_5$. *M* 367.39. Calculated, %: C 68.65; H 5.76; N 3.81.

**Methyl 3-(4-bromophenyl)aminocarbonyl-5-(4-methylphenyl)-5-oxo-3(*Z*)-pentenoate (IId).** Yield 1.45 g (70%), mp 157–158°C (from ethanol). IR spectrum, ν, $cm^{-1}$: 3338 (CO*NH* amide), 1753 ($C^1$=O ester), 1680–1690 (*CO*NH amide, 4-$CH_3C_6H_4COCH$=). UV spectrum, $\lambda_{max}$ (log ε), nm: 226 (4.17), 313 (3.56). $^1$H NMR spectrum, acetone-$d_6$, δ, ppm: 2.24 s (3H, $CH_3$), 3.41 s (2H, $C^2H_2$), 3.68 s (3H, $OCH_3$ in $COOCH_3$), 6.38 s (1H, $C^4H$), 6.90–7.76 m (8H, $2C_6H_4$), 7.40 s (1H, NH). $^1$H NMR spectrum, DMSO-$d_6$, δ, ppm: 2.18 s (3H, $CH_3$), 3.41 s (2H, $C^2H_2$), 3.62 s (3H, $OCH_3$ in $COOCH_3$), 6.94 s (1H, $C^4H$), 7.16–7.63 m (8H, $2C_6H_4$), 7.42 s (1H, NH). Found, %: C 57.54; H 4.52; Br 19.12; N 3.17. $C_{20}H_{18}BrNO_4$. *M* 416.27. Calculated, %: C 57.71; H 4.36; Br 19.20; N 3.36.

**Methyl 3-(4-methoxyphenyl)aminocarbonyl-5-oxo-5-(4-chlorophenyl)-3(*Z*)-pentenoate (IIe).** *b*. A mixture of 1.04 g (5 mmol) of 5-(4-chlorophenyl)-furan-2,3-dione (**VIII**) and 0.62 g (5 mmol) of *p*-anisidine was heated for 3–5 min with stirring in 50 ml of benzene, then was added 1.67 g (5 mmol) of methyl triphenylphosphoraylideneacetate, heating with stirring was continued till dissolving, then the mixture was refluxed for 0.5 h. Solvent was evaporated and residue was carefully grinded with hexane and ether and recrystallized from ethanol and then from acetonitrile. From the residual solution was isolated triphenylphosphine oxide, yield 0.86 g (62%), mp 156–157°C (from tetrachloromethane). Compound **IIe**: method *a*, yield 1.61 g (83%); method *b*, yield 1.10 g (57%), mp 166–167°C (from acetonitrile). IR spectrum, ν, $cm^{-1}$: 3350 (CO*NH* amide), 1744 ($C^1$=O ester), 1672–1683 (*CO*NH amide, 4-$ClC_6H_4COCH$=). $^1$H NMR spectrum, $CDCl_3$, δ, ppm: 3.35 s (2H, $C^2H_2$), 3.71 s (3H, $CH_3O$ in 4-$CH_3OC_6H_4$), 3.75 s (3H, $OCH_3$ in $COOCH_3$), 4.77 s (1H, $C^4H$), 6.65–7.35 m (8H, $2C_6H_4$), 7.24 s (1H, NH). Found, %: C 61.85; H 4.51; Cl 9.19; N 3.84. $C_{20}H_{18}ClNO_5$. *M* 387.81. Calculated, %: C 61.94; H 4.68; Cl 9.14; N 3.61.

**Ethyl 5-(4-bromophenyl)-3-(4-methylphenyl)-aminocarbonyl-5-oxo-3(*Z*)-pentenoate (IIf).** Yield 1.65 g (77%), mp 147–148°C (from ethanol). IR spectrum, ν, $cm^{-1}$: 3338 (CO*NH* amide), 1747 ($C^1$=O ester), 1677–1685 (*CO*NH amide, 4-$BrC_6H_4COCH$=). UV spectrum, $\lambda_{max}$ (log ε), nm: 228 (4.28), 331 (3.34). $^1$H NMR spectra, acetone-$d_6$, δ, ppm: 1.21 t (3H, $CH_3$ in $COOC_2H_5$, *J* 7.2 Hz), 2.17 s (3H, $CH_3$ in 4-$CH_3C_6H_4$), 3.36 s (2H, $C^2H_2$), 4.13 q (3H, $CH_2$ in $COOC_2H_5$, *J* 7.0 Hz), 6.31 s (1H, $C^4H$), 6.88–7.45 m (8H, $2C_6H_4$), 7.40 s (1H, NH). $^1$H NMR spectrum, DMSO-$d_6$, δ, ppm: 1.19 t (3H, $CH_3$ in $COOC_2H_5$, *J* 7.2 Hz), 2.17 s (3H, $CH_3$ in 4-$CH_3C_6H_4$), 3.42 s (2H, $C^2H_2$), 4.11 q (3H, $CH_2$ in $COOC_2H_5$, *J* 7.0 Hz), 6.92 s (1H, $C^4H$), 7.02–7.58 m (8H, $2C_6H_4$), 7.42 s (1H, NH). Found, %: C 58.49; H 4.84; Br 18.49; N 3.39. $C_{21}H_{20}BrNO_4$. *M* 430.29. Calculated, %: C 58.62; H 4.68; Br 18.57; N 3.26. Mass spectrum, *m/z* ($I_{rel}$, %), the ions with $I_{rel}$ > 4% (besides molecular ions) are listed: 431 (0.5) [*M* ($^{81}$Br isotope)]$^+$, 429 (0.6) [*M* ($^{79}$Br isotope)]$^+$; 385 (5), 383 (4) [*M* – $OC_2H_5$ – H]$^+$; 357 (6), 355 (6) [*M* – $OC_2H_5$ – H – CO]$^+$; 341 (7), 339 (7); 340 (5), 338 (4) [*M* – 4-$CH_3$·$C_6H_4]^+$; 325 (17), 323 (17) [*M* – 4-$CH_3C_6H_4NH]^+$; 322 (9); 296 (10), 294 (10) [*M* – 4-$CH_3C_6H_4NH$ – CO – H]$^+$ or [4-$BrC_6H_4CO$–CH=C=CH–$COOC_2H_5]^+$; 279 (21), 277 (21) [*M* – 4-$CH_3C_6H_4NH$ – $OC_2H_5$ – H]$^+$ or [4-$BrC_6H_4CO$–CH=C(C=O)–CH=C=O]$^+$; 268 (7), 266 (7); 252 (10), 250 (10) or $[C_{11}H_7BrO_2]^+$; 251 (9), 249 (8) [*M* – 4-$CH_3C_6H_4NH$ – CO – $OC_2H_5$ – H]$^+$ or $[C_{11}H_6BrO_2]^+$; 200 (5); 186 (7), 184 (7); 185 (89), 183 (90) [4-$BrC_6H_4$-C≡O]$^+$; 172 (8); 157 (29), 155 (30) [4-$BrC_6H_4]^+$; 144 (15); 133 (4) [4-$CH_3C_6H_4$–N=C=O]$^+$; 132 (5); 128 (5); 126 (7); 116 (5); 115 (10); 114 (5); 107 (100) [4-$CH_3C_6H_4NH_2]^+$; 106 (82) [4-$CH_3C_6H_4NH]^+$; 105 (5); 104 (12); 91 (18) [4-$CH_3C_6H_4]^+$; 83 (5); 79 (11); 78 (8); 77 (22) $[C_6H_5]^+$; 76 (23); 75 (17); 74 (5); 73 (5); 71 (6), 69 (6); 67 (9); 65 (10); 63 (6); 60 (4), 57 (10); 55 (9); 53 (6); 52 (6); 51 (9); 50 (12); 46 (5); 45 (16); 44 (6); 43 (10). Found, %: C 61.47; H 4.30; N 9.23. $C_{16}H_{14}N_2O_5$. *M* 314.29. Calculated, %: C 61.14; H 4.49; N 8.91.

**Adduct (1 : 1) of methyl 5-oxo-5-phenyl-3-phenylaminocarbonyl-3(*Z*)-pentenoate with triphenylphosphine oxide (III).** Yield 2.35 g (78%), mp 105–106°C (from ethanol). IR spectrum, ν, $cm^{-1}$: 3210 (CO*NH* amide), 1746 ($C^1$=O ester), 1675–1692 (*CO*NH amide, $C_6H_5COCH$=). $^1$H NMR spectrum, acetone-$d_6$, δ, ppm: 3.25 s (2H, $C^2H_2$), 3.52 s (3H, $OCH_3$ in $COOCH_3$), 6.88 s (1H, $C^4H$), 7.15–7.95 m (26H, $5C_6H_5$, NH). Found, %: C 73.65; H 5.49; N 2.18. $C_{37}H_{32}NO_5P$. *M* 601.63. Calculated, %: C 73.87; H 5.36; N 2.33.

**2-Hydroxy-4-oxo-4-phenyl-2(*Z*)-butenic (4-methylphenyl)amide (Ia).** mp 132–133°C (from toluene). Published: mp 123–124°C [22]. $^1$H NMR spectra, $CDCl_3$, δ, ppm: 2.26 s (3H, $CH_3$), 4.55 s (2H, $C^3H_2$, β-diketone form **B**, 1.5%), 7.10 s (1H, $C^3H$, enol form **A**, 98.5%), 7.20–8.03 m (9H, $C_6H_5$, $C_6H_4$), 9.02 br.s (1H, NH), 14.58 br.s (1H, OH).

**4-(4-Bromophenyl)-2-hydroxy-4-oxo-2(*Z*)-butenic (4-methylphenyl)amide (If).** mp 154–155°C (from toluene) [26]. $^1$H NMR spectrum, DMSO-$d_6$, δ, ppm: 2.28 s (3H, $CH_3$), 4.62 s (2H, $C^3H_2$, form **B**, 7.2%), 7.13 s (1H, $C^3H$, form **A**, 92.8%), 7.25–8.12 m (8H, $2C_6H_4$), 10.58 br.s (1H, NH).

**2-Hydroxy-4-oxo-4-phenyl-2(*Z*)-butenic phenylamide (Ig).** mp 114–115°C (from ethanol). Published: mp 113–114°C [22], 124–125°C [26, 27]. $^1$H NMR spectrum, DMSO-$d_6$, δ, ppm: 4.60 s (2H, $C^3H_2$, form **B**, 9.7%), 7.12 s (1H, $C^3H$, form **A**, 90.3%), 7.15–8.07 m (10H, $2C_6H_5$), 10.37 br.s (1H, NH).

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