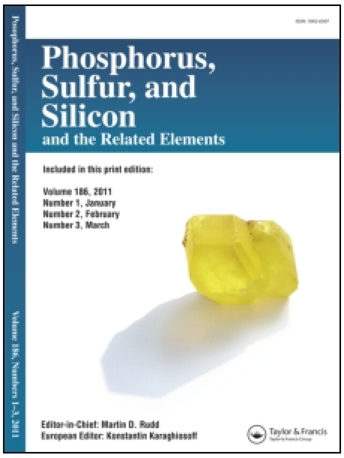

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OXALYLMETHYLENEPHOSPHORANES. 1. REACTIONS OF ETHYL TRIPHENYLPHOSPHORANYLIDENEPYRUVATE AND TRIPHENYLPHOSPHORANYLIDENEPYRUVIC ACID HYDRAZIDE WITH 5-ARYL-2,3-FURANDIONES

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OXALYLMETHYLENEPHOSPHORANES. 1. REACTIONS OF ETHYL TRIPHENYLPHOSPHORANYLIDENEPYRUVATE AND TRIPHENYLPHOSPHORANYLIDENEPYRUVIC ACID HYDRAZIDE WITH 5-ARYL-2,3-FURANDIONES

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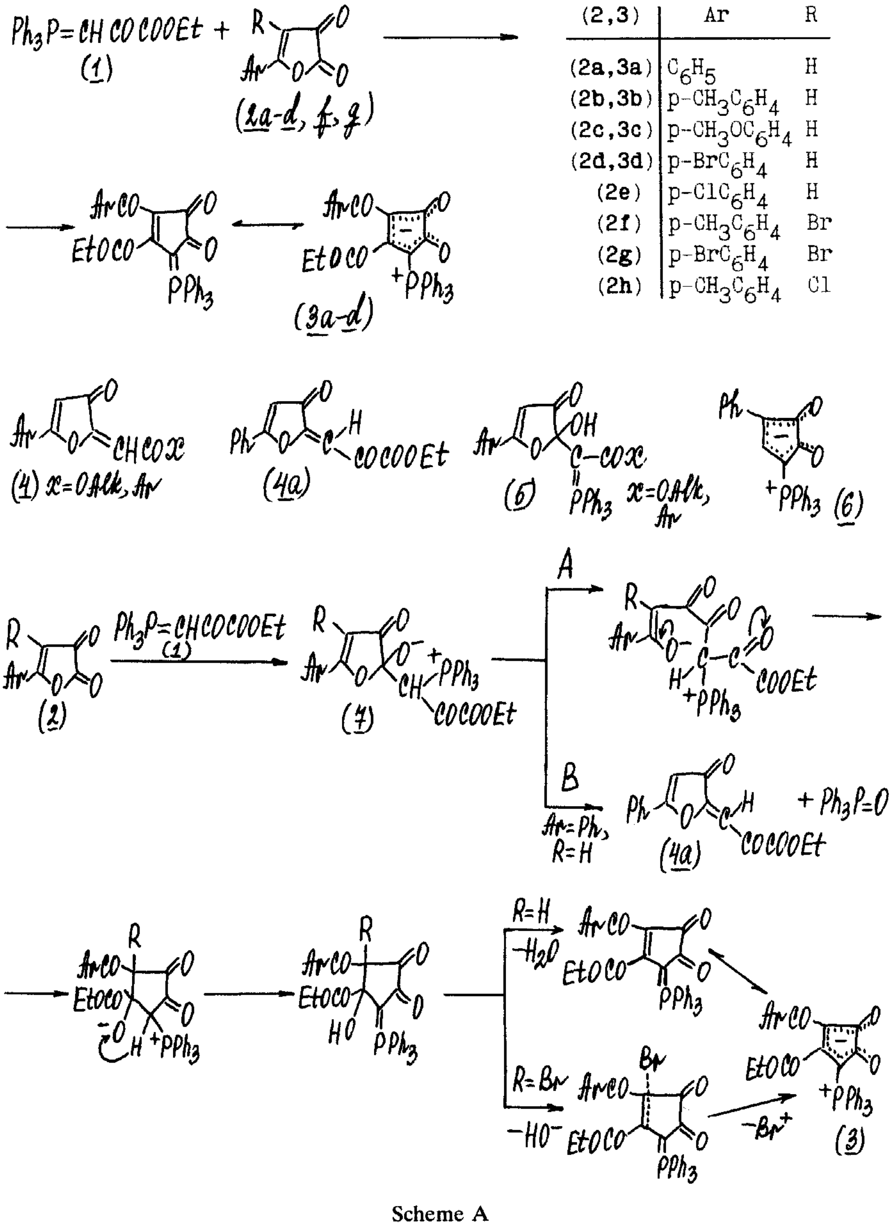
Ethyl triphenylphosphoranylidenepyruvate (**1**) readily reacts with 5-aryl-2,3-furandiones (**2**) to afford the deeply coloured resonance stabilized cyclic oxalyl ylides (**3**) being inactive towards aldehydes. Once a small amount of the competitive Wittig product - 2-ethoxalyl-5-phenyl-3(2H)-furanone (**4a**) besides the corresponding phosphorane (**3a**) has been obtained. However triphenylphosphoranylidenepyruvic acid hydrazide (**8**) when treated with 5-aryl-2,3-furandiones (**2**) gives only aroylpyruvoylhydrazides (**10**), which can be converted to 3-pyrazolcarboxylic acid hydrazides (**13**). A possible mechanism of the reaction of ylide (**1**) with 2,3-furandiones (**2**) is proposed.

Key words: Ethyl triphenylphosphoranylidenepyruvate; triphenylphosphoranylidenepyruvic acid hydrazide; reactions with 5-aryl-2,3-furandiones; 1-triphenylphosphoranylidene-4-cyclopentene-2,3-diones; oxalyl ylides; reactivity towards carbonyl reagents.

INTRODUCTION

Among the well known acylmethylenephosphoranes only monocarbonyl and β-dicarbonyl (diacyl) ylides are widely used in organic synthesis mainly as versatile Wittig reagents.[2] But a few data have earlier been reported on the synthetic applications of α-dicarbonyl compounds of this series.[3–6] Our interest has been directed towards oxalylmethylenephosphoranes[4–6] as olefinating reagents to construct new types of important oxalyl compounds of expected biological activity. These ylides may also have an interest for the thermolysis reactions giving acyl substituted acetylenes.[6] We have found only four reports on the Wittig reaction of ethoxalyl- or oxamoylmethylenetriphenylphosphoranes with some aliphatic and aromatic aldehydes,[5] galactose derivatives[4] or ethyl pyruvate[5] besides our preliminary studies.[7] No research data except with ethyl pyruvate have ever been published on the reaction of oxalylmethylenephosphoranes with ketones or oxoesters, or cyclic oxocompounds.

Recently we have examined the Wittig reaction of alkoxycarbonyl- and aroylmethylenetriphenylphosphoranes with 5-aryl-2,3-furandiones (**2**) which proceeded regiospecifically to afford 2-acylmethylene-5-aryl-3(2H)-furanones (**4**), with the heterocyclic oxalyl ylides - 5-aryl-2-hydroxy-2-triphenylphosphoranylidenemethyl-3(2H)-furanones (**5**) being the reactive intermediates.[8] To obtain more information on the interaction of 2,3-furandiones (**2**) with acylmethylenephosphoranes we have



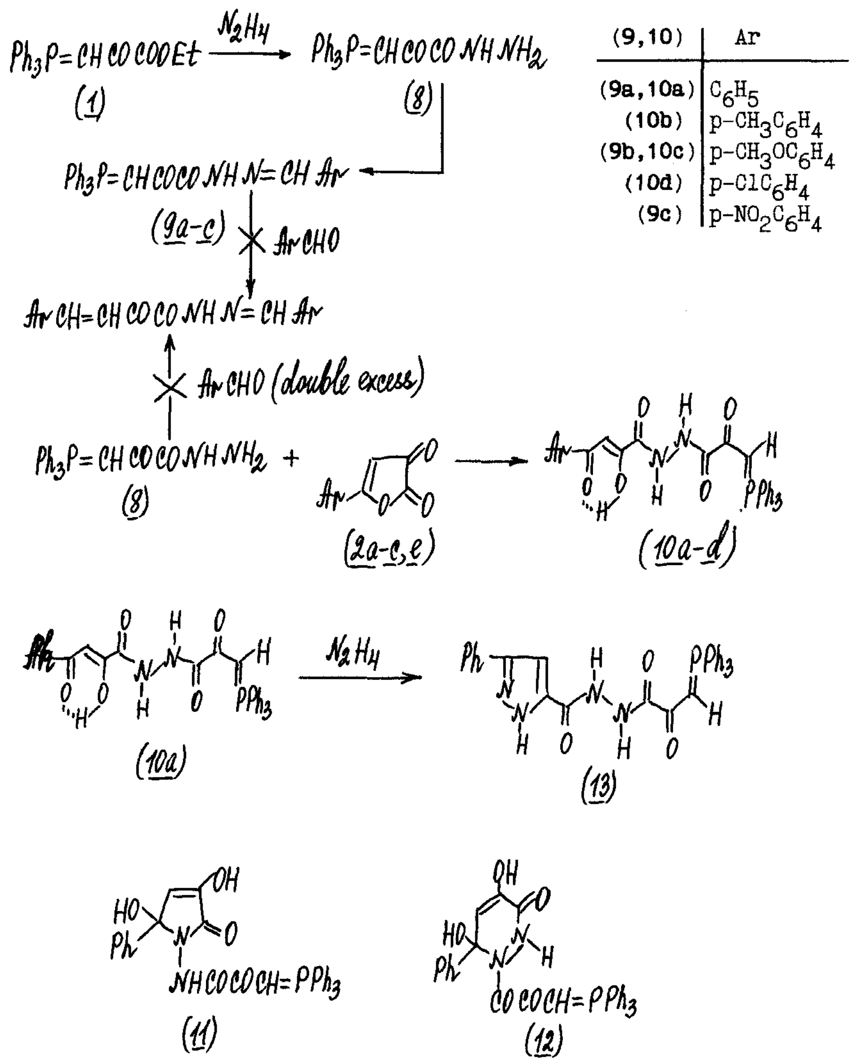
(2,3)	Ar	R
(2a,3a)	C_6H_5	H
(2b,3b)	p-$CH_3C_6H_4$	H
(2c,3c)	p-$CH_3OC_6H_4$	H
(2d,3d)	p-BrC_6H_4	H
(2e)	p-ClC_6H_4	H
(2f)	p-$CH_3C_6H_4$	Br
(2g)	p-BrC_6H_4	Br
(2h)	p-$CH_3C_6H_4$	Cl

Scheme A

investigated the reaction of ethyl triphenylphosphoranylidenepyruvate (**1**) and the newly synthesized triphenylphosphoranylidenepyruvic acid hydrazide (**8**) with 5-aryl-2,3-furandiones (**2a–h**).

RESULTS AND DISCUSSION

On studying the reaction of ethyl triphenylphosphoranylidenepyruvate (**1**) with 5-aryl-2,3-furandiones (**2a–d**), carried out by brief heating in benzene we have



(9,10)	Ar
(9a,10a)	C_6H_5
(10b)	$p-CH_3C_6H_4$
(9b,10c)	$p-CH_3OC_6H_4$
(10d)	$p-ClC_6H_4$
(9c)	$p-NO_2C_6H_4$

Scheme B

found that unexpectedly deep violet compounds were formed. The latter appeared to have one phosphorus atom in the molecule, and the detailed investigation of the structure proved them to be the resonance stabilized cyclic oxalyl ylides - 4-aroyl-5-ethoxycarbonyl-1-triphenylphosphoranylidene-4-cyclopentene-2,3-diones (**3a–d**) (see Scheme A). As compared with the earlier reported 1-phosphoranylidene-4-cyclopentene-2,3-dione (**6**)[9] the structure of the synthesized compounds is supported by spectroscopic methods. Together with the corresponding ylide (**3a**) derived from the reaction of phosphorane (**1**) with 2,3-furandione (**2a**) a small amount (18%) of 2-ethoxalyl-5-phenyl-3(2H)-furanone (**4a**) besides triphenylphosphine oxide has been obtained. Treatment of phosphorane (**1**) with 4-bromo substituted 2,3-furandiones (**2f,g**) under similar conditions gives the same ylides (**3b,d**); but when the 4-chloro derivative (**2h**) was used only resinous black residue has been obtained which could not be identified. The following reaction mechanism is thus assumed (Scheme A). We think that the phosphobetaines (**7**) probably formed as a result of C-nucleophilic attack of ylide (**1**) on the C-2 atom of 2,3-furandiones (**2**) may be involved through several steps in a competition process to afford mainly recyclization products which represent the major new resonance stabilized ylides (**3**), or to a minor extent Wittig olefines by triphenylphosphine oxide elimination. When the substituent *R* is an easily leaving bromine atom the latter comes off in the presence of traces of water.

Attempts to use the cyclic phosphorus ylides (**3**) like the known parent phosphoranes (**6**)[9] in the Wittig reaction with benzaldehyde or *p*-nitrobenzaldehyde have unfortunately failed; this is probably due to the extreme stability of the P=C bond of the compounds (**3**) towards carbonyl reagents.

Of much importance would also appear to be the reaction possibilities of oxalylmethylenephosphoranes having additional nucleophilic fragments in the molecule. Such an opportunity seemed to be present in the new stable triphenylphosphoranylidenepyruvic acid hydrazide (**8**) which can be synthesized by treatment of ylide (**1**) with hydrazine hydrate in ethanol solution (Scheme B). The hydrazide (**8**) does not react with acetone, but aromatic aldehydes readily react with compound (**8**) to afford the corresponding triphenylphosphoranylidenepyruvic acid arylidenehydrazides (**9a–c**).

No possible Wittig olefines were thus observed either at double excess of aldehyde or by the reaction of the latter with the separated compounds (**9**).

Reaction of 5-aryl-2,3-furandiones (**2a–c,e**) with the ylide (**8**) proceeds similarly to give the triphenylphosphoranylidenepyruvic acid aroylpyruvoylhydrazides (**10a–d**), existing as H-chelate tautomers both in crystals and solution. This fact is proved by a low value of the IR carbonyl frequency for aroylpyruvic fragment of compounds (**10**) at 1568–1595 cm^{-1} as well as an absence of a high field ^1H NMR signals of the CH_2 groups. These data are supported by the known stabilized chelate structure of aroylpyruvic acid derivatives, such as aroylpyruvic acid β-aroylhydrazides.[10] The availability of benzoylketene ion m/e 146 in the mass spectrum of the compound (**10a**) lacking the corresponding benzonitrile ion m/e 103 makes it possible to exclude the alternative structures of 2-pyrrolone (**11**) and 3-pyridazinone (**12**) O,N-semiacetals.

No changes of the acyl ylide fragment of compound (**10a**) however do we observe on treatment with hydrazine hydrate instead heterocyclization of the benzoylacetyl fragment occurs to afford triphenylphosphoranylidenepyruvic acid 5-phenyl-3-pyrazolylcarbonylhydrazide (**13**).

CONCLUSION

It has been demonstrated that oxalylmethylenetriphenylphosphoranes (**1**) or (**8**) can be used in the reaction with 5-aryl-2,3-furandiones (**2**) giving either ylides (**3**), being the competitive recyclization products, and regioisomeric (by lactone carbonyl of the starting 2,3-furandione) Wittig olefines (**4**), or the aroylacylated phosphoranes (**10**) depending on the nucleophilic properties of the starting ylide. The syntheses of new types of oxalyl ylides as well as the studies of their reactions with oxocompounds are underway.

EXPERIMENTAL

Melting points were determined without correction on a PTP Capillary Melting Point Apparatus (Russia). Elemental analyses were carried out in the Laboratory for Microanalysis of Perm Pharmaceutical Institute. IR spectra were recorded on a Zeiss Specord M-80 spectrometer using standard polystyrene film. Ultraviolet spectrum of the compound (**4a**) was obtained with a Specord UV-Vis spectrometer, ethanol concentration being 10^{-4} mol%. NMR spectra were recorded on a RS-60 or Bruker HX-90 spectrometer using $CDCl_3$, DMSO-D_6, $CDCl_3$-CF_3COOH (10:1), and DMSO-D_6 -CF_3COOH (10:1) mixture as solvents. Chemical shifts are reported in parts per million (δ scale) using HMDS (adding 0.05 ppm upon measuring) and 85% H_3PO_4 (^{31}P) as internal standards. Low-resolution mass spectra were obtained with a Varian MAT-311 (70 eV) instrument. TLC on silica gel plates Silufol UV-254 was used to follow the reactions and to check the purity of products, eluent being benzene-diethyl ether (3:2), or benzene-diethyl ether-acetone (10:9:1) mixture, visualization done with iodine or ultraviolet light as appropriate. Benzene, toluene and dioxane were distilled from sodium metal, acetone-from tetraphosphorus decaoxide prior to use. The phosphorane (**1**) was prepared by the known method.[4,5] 5-Aryl-2,3-furandiones (**2a–e**) were prepared as previously described.[11]

Reaction of Ethyl Triphenylphosphoranylidenepyruvate (**1**) *with 5-Aryl-2,3-furandiones* (**2a–d**). General Procedure. A mixture of ethyl triphenylphosphoranylidenepyruvate (**1**)[4,5] (3.76 g, 10 mmol) and the appropriate 5-aryl-2,3-furandiones (**2a–d,f–h**)[11] (10 mmol) in benzene (100 ml) was refluxed for 3–5 min. After removal of the solvent, the resinous residue was allowed to stay at room temperature for about 3–5 days. The product was washed with benzene or toluene (30–50 ml) and crystallized from ethanol to give the compounds (**3a–d**) as deep violet crystals.

When the starting compound (**2h**) was allowed to react with ylide (**1**) only a black resinous residue has been obtained. TLC technique was used to follow the reaction, and traces of triphenylphosphine oxide were detected also.

4-Benzoyl-5-ethoxycarbonyl-1-triphenylphosphoranylidene-4-cyclopentene-2,3-dione (**3a**) *and 2-Ethoxalyl-5-phenyl-3(2H)-furanone* (**4a**). By the general procedure, reaction of the compound (**1**) (3.76 g, 10 mmol) with 2,3-furandione (**2a**) (1.74 g, 10 mmol) gave the ylide (**3a**), yield 3.78 g (71%), mp. 269–270°C. IR (NaCl, cm^{-1}): 1744 (COOEt), 1688 (COAr) 1615, 1595 (CO cycle), 1454 (P—C_6H_5), 1230 (P═C). ^1H NMR ($CDCl_3$, δ): 1.02 (t, 3H, CH_3CH_2O), 3.46 (q, 2H, CH_3CH_2O), 7.20–7.80 (m, 20H, 4Ph). Mass-spectrum, m/e: 277 [$Ph_3PO^{\cdot+}$], 262 [$Ph_3P^{\cdot+}$], 202 [PhCO—C≡C—COOEt$^{\cdot+}$], 201 [Ph_2PO^+], 185 [Ph_2P^+], 108 [PhP^+], 105 [$PhCO^+$], 77 [Ph^+], 47 [P═O^+]. Anal. Calcd. for: $C_{33}H_{25}O_5P$: C, 74.43; H, 4.69; Found: C, 74.58; H, 4.76.

Further treatment of the remaining residue with benzene (100 ml) followed by column chromatography on aluminium oxide, benzene as eluent, gave after crystallization from ethanol orange crystals of compound (**4a**); yield 0.25 g (18%), mp. 132–133°C. IR (NaCl, cm^{-1}): 1732 (COOEt), 1690, 1665 (COCOOEt, CO cycle), 1609 (C═C, Ar). UV [ethanol, λ, nm (lg ε)]: 209 (4.15), 227 (4.04), 306 (4.09), 368 (3.90). ^1H NMR ($CDCl_3$, δ): 1.28 (t, 3H, CH_3CH_2O), 4.31 (q, 2H, CH_3CH_2O), 6.25 (s, 1H, CH exo), 6.84 (s, 1H, CH cycle), 7.40–7.95 (m, 5H, Ph). Anal. Calcd. for: $C_{15}H_{12}O_5$: C, 66.18; H, 4.44; Found: C, 66.37; H, 4.52.

Heating of the equimolar (2 mmol) mixture of the compound (**3a**) (1.07 g) with benzaldehyde or *p*-nitrobenzaldehyde in dioxane under reflux for 20 hours gave the starting reactants unchanged (TLC control used).

4-p-Methylbenzoyl-5-ethoxycarbonyl-1-triphenylphosphoranylidene-4-cyclopentene-2,3-dione (**3b**). Yield 86% [from the starting 5-*p*-tolyl-2,3-furandione (**2b**)] or 34% [from the 4-bromo-5-*p*-tolyl-2,3-furandione (**2f**)], mp. 243–244°C. IR (NaCl, cm^{-1}): 1739 (COOEt), 1695 (COAr), 1620, 1608 (CO cycle), 1452 (P—C_6H_5), 1235 (P═C). ^1H NMR (DMSO-d_6, δ): 1.02 (t, 3H, CH_3CH_2O), 3.35 (s, 3H, CH_3), 3.50 (q, 2H, CH_3CH_2O), 7.35–7.75 (m, 19H, 3Ph, C_6H_4). ^{31}P NMR (300 MHz, DMSO, δ): +8.99. Anal. Calcd. for: $C_{34}H_{27}O_5P$: C, 74.72; H, 4.98; Found: C, 74.78; H, 5.11.

4-p-Methoxybenzoyl-5-ethoxycarbonyl-1-triphenylphosphoranylidene-4-cyclopentene-2,3-dione (**3c**). Yield 80%, mp. 241–242°C. IR (NaCl, cm^{-1}): 1742 (COOEt), 1683 (COAr), 1617, 1609 (COcycle), 1449 (P—C_6H_5), 1240 (P═C). ^1H NMR ($CDCl_3$, δ): 1.03 (t, 3H, CH_3CH_2O), 3.45 (q, 2H, CH_3CH_2O), 3.62 (s, 3H, CH_3O), 7.45–7.88 (m, 19H, 3Ph, C_6H_4). Anal. Calcd. for: $C_{34}H_{27}O_6P$: C, 72.59; H, 4.84; Found: C, 72.63; H, 4.71.

4-p-Bromobenzoyl-5-ethoxycarbonyl-1-triphenylphosphoranylidene-4-cyclopentene-2,3-dione (**3d**). Yield 75% [from the starting compound (**2d**)] or 47% [from the compound (**2g**)], mp. 129–130°C. IR (NaCl, cm^{-1}): 1728 (COOEt), 1692 (COAr), 1596 (CO cycle), 1420 (P—C_6H_5), 1245 (P═C). ^1H NMR ($CDCl_3$, δ): 1.03 (t, 3H, CH_3CH_2O), 3.53 (q, 2H, CH_3CH_2O), 7.40–7.75 (m, 19H, 3Ph, C_6H_4). Anal. Calcd. for: $C_{33}H_{24}BrO_5P$: C, 64.83; H, 3.96; Found: C, 65.09; H, 4.12.

Triphenylphosphoranylidenepyruvic acid hydrazide (**8**). To a solution of ethyl triphenylphosphoranylidenepyruvate (**1**) (3.76 g, 10 mmol) in ethanol (80 ml) 70% hydrazine (1.0 ml) was added, and the mixture was refluxed for 3 hours. After removal of the solvent, the residue was crystallized from ethanol-water (1:1) to give the ylide (**8**), yield 2.60 g (72%), mp. 229–230°C. IR (NaCl, cm^{-1}): 3395, 3345–3360 (NH$_2$, NH), 1663 ($\underline{\text{CO}}$NH), 1615 (P$\overset{\cdots}{-}$C$\overset{\cdots}{-}$C$\overset{\cdots}{-}$O), 1442, 1470–1480 (P—Ph). ^{1}H NMR (DMSO-d$_6$, δ): 4.24 (unresolved, 2H, NH$_2$), 7.45–7.85 (m, 16H, 3Ph, P=$\underline{\text{CH}}$), 9.15 (broad, 1H, NH). Anal. Calcd. for: $C_{21}H_{19}N_2O_2P$: C, 69.61; H, 5.29; N, 7.73; Found: C, 69.50; H, 5.13; N, 7.85.

From the mother liquors a small amount of oxalic acid dihydrazide, H$_2$NNHCOCONHNH$_2$, was isolated, yield 0.2 g (17%), mp. 241–242°C dec. (lit.[12] 243°). IR (NaCl, cm^{-1}): 3275–3305, 3195 (CO$\underline{\text{NHNH}_2}$), 1665, 1649 ($\underline{\text{CO}}$NH), 1605–1615. Mass-spectrum, m/e ($I \geqslant 3\%$): 118 (49)[M$^{\cdot+}$], 100 (3) [M-H$_2$O$^+$], 90(3)[M-CO$^{\cdot+}$], 59 (11)[H$_2$NNHCO$^+$], 58 (4), 45 (3), 44 (8)[H$_2$NCO$^+$], 43 (7) [NHCO$^+$], 32 (100)[H$_2$N-NH$_2^{\cdot+}$], 31 (43), 30 (8), 29 (10).

Heating of compound (**8**) (0.72 g, 2 mmol) in acetone solution under reflux for 50 hours gave the starting ylide unchanged (TLC control used).

Reaction of Triphenylphosphoranylidenepyruvic Acid Hydrazide (**8**) *with Aromatic Aldehydes. Synthesis of Triphenylphosphoranylidenepyruvic Acid Arylidenehydrazides* (**9a–c**). General Procedure. A mixture of the ylide (**8**) (0.91 g, 2.5 mmol) and the appropriate aromatic aldehydes (2.5 mmol) in ethanol (50 ml) was refluxed for 1–2 hours. The precipitate was then collected, washed with ethanol and crystallized from dichloroethane (**9a**) or benzene (**9b,c**) to give the desired pure compounds (**9a–c**).

Triphenylphosphoranylidenepyruvic Acid Benzylidenehydrazide (**9a**). Yield 0.80 g (71%), mp. 256–257°C dec. IR (NaCl, cm^{-1}): 3215 (CO$\underline{\text{NH}}$), 1668 ($\underline{\text{CO}}$NH), 1585 (P$\overset{\cdots}{-}$C$\overset{\cdots}{-}$C$\overset{\cdots}{-}$O), 1440 (P—Ph), 1195 (P=C). ^{1}H NMR (DMSO-d$_6$, δ): 7.23–7.95 (m, 22H, 4Ph, CH, P=$\underline{\text{CH}}$), 11.60 (s, 1H, $\underline{\text{NH}}$CO). Anal. Calcd. for: $C_{28}H_{23}N_2O_2P$: C, 74.66; H, 5.15; N, 6.22; Found: C, 74.78; H, 5.06; N, 6.31. Heating of the ylide (**9a**) (0.90 g, 2 mmol) with the equimolar amount (0.3 g) of *p*-nitrobenzaldehyde in dioxane (50 ml) under reflux for 5 hours gave the starting reactants unchanged.

Triphenylphosphoranylidenepyruvic Acid p-*Methoxybenzylidenehydrazide* (**9b**). Yield 1.15 g (96%), mp. 225–226°C dec. IR (NaCl, cm^{-1}): 3264 (CO$\underline{\text{NH}}$), 1690 ($\underline{\text{CO}}$NH), 1608 (P$\overset{\cdots}{-}$C$\overset{\cdots}{-}$C$\overset{\cdots}{-}$O). ^{1}H NMR (DMSO-d$_6$, δ): 3.77 (s, 3H, CH$_3$O), 7.08 (s, 1H, $\overline{\text{CH}}$), 7.35–8.25 (m, 20H, 3Ph, C$_6$H$_4$, P=$\underline{\text{CH}}$), 11.47 (s, 1H, $\underline{\text{NH}}$CO). Anal. Calcd. for: $C_{29}H_{25}N_2O_3P$: C, 72.49; H, 5.24; N, 5.83; Found: C, 72.64; H, 5.37; N, 5.98.

Triphenylphosphoranylidenepyruvic Acid p-*Nitrobenzylidenehydrazide* (**9c**). Yield 0.48 g (39%), mp. 235–236°C dec. IR (NaCl, cm^{-1}): 3205 (CO$\underline{\text{NH}}$), 1678 ($\underline{\text{CO}}$NH), 1590 (P$\overset{\cdots}{-}$C$\overset{\cdots}{-}$C$\overset{\cdots}{-}$O), 1475 (P=Ph), 1243 (P=C). ^{1}H NMR (DMSO-d$_6$, δ): 7.32 (s, 1H, CH), 7.28–7.80 (m, 20H, 3Ph, C$_6$H$_4$, P=$\underline{\text{CH}}$). Anal. Calcd. for: $C_{28}H_{22}N_3O_4P$: C, 67.88; H, 4.47; N, 8.48; Found: C, 67.71; H, 4.50; N, 8.58.

Reaction of Triphenylphosphoranylidenepyruvic Acid Hydrazide (**8**) *with 5-Aryl-2,3-furandiones* (**2a–c,e**). *Synthesis of Triphenylphosphoranylidenepyruvic Acid Aroylpyruvoylhydrazides* (**10a–d**). General Procedure. A mixture of the ylide (**8**) (1.81 g, 5 mmol) and the appropriate 5-aryl-2,3-furandiones (**2a–c,e**) (5 mmol) in benzene (80 ml) was heated under reflux until the solid dissolved (2–3 min). After cooling the precipitate was collected and crystallized from chloroform-hexane (3:1) to give the pure compounds (**10a–d**).

Triphenylphosphoranylidenepyruvic Acid Benzoylpyruvoylhydrazide (**10a**). Yield 79%, mp. 212–213°C dec. IR (NaCl, cm^{-1}): 3205–3215 (CO$\underline{\text{NH}}$), 1687, 1658 ($\underline{\text{CO}}$NH), 1558–1595 (CO chelate, P$\overset{\cdots}{-}$C$\overset{\cdots}{-}$C$\overset{\cdots}{-}$O). ^{1}H NMR (DMSO-d$_6$, δ): 7.27–7.70 (m, 21H, 4Ph, P=$\underline{\text{CH}}$). Mass-spectrum, *m/e* ($I \geqslant 3\%$): 361 (3) [Ph$_3$P=CHCOCONHNH$^+$], 303 (11) [Ph$_3$P=CH—C≡O$^+$], 278 (22) [Ph$_3$P=O$^{\cdot+}$], 262 (4) [Ph$_3$P$^{\cdot+}$], 201 (6) [Ph$_2$P$^+$], 174 (7) [PhCOCH$_2$COC≡NH$^+$], 146 (11) [PhCOCH=C=O$^{\cdot+}$], 119 (7) [PhCOCH$_2^{\cdot+}$], 105 (46) [PhCO$^+$], 77 (35) [Ph$^+$], 58 (100) [H$_2$N—N=C=O$^{\cdot+}$], 57 (63) [HN=N—C≡O$^+$], 43 (72) [HNCO$^{\cdot+}$]. Anal. Calcd. for: $C_{31}H_{25}N_2O_5P$: C, 69.40; H, 4.70; N, 5.22; Found: C, 69.57; H, 4.85; N, 5.13.

Triphenylphosphoranylidenepyruvic Acid p-*Methylbenzoylpyruvoylhydrazide* (**10b**). Yield 72%, mp. 203–204°C dec. IR (NaCl, cm^{-1}): 3215–3225 (CO$\underline{\text{NH}}$), 1696, 1660 ($\underline{\text{CO}}$NH), 1595, 1568 (CO chelate, P$\overset{\cdots}{-}$C$\overset{\cdots}{-}$C$\overset{\cdots}{-}$O). ^{1}H NMR (DMSO-d$_6$, δ): 2.31 (s, 3H, CH$_3$), 7.05–7.70 (m, 20H, 3Ph, C$_6$H$_4$, P=$\underline{\text{CH}}$). Anal. Calcd. for: $C_{32}H_{27}N_2O_5P$: C, 69.81; H, 4.94; N, 5.09; Found: C, 69.90; H, 4.79; N, 5.27.

Triphenylphosphoranylidenepyruvic Acid p-*Methoxybenzoylpyruvoylhydrazide* (**10c**). Yield 84%, mp. 218–219°C dec. IR (NaCl, cm^{-1}): 3365, 3408 (CO$\underline{\text{NH}}$), 1702, 1680 ($\underline{\text{CO}}$NH), 1595, 1580 (CO chelate, P$\cdots$C$\cdots$C$\cdots$O). ^{1}H NMR (DMSO-d$_6$, δ): 3.96 (s, 3H, CH_3O), 7.08–8.00 (m, 20H, 3Ph, C_6H_4, P=$\underline{\mathrm{CH}}$). Anal. Calcd. for: $C_{32}H_{27}N_2O_6P$: C, 67.84; H, 4.80; N, 4.94; Found: C, 67.60; H, 4.97; N, 5.16.

Triphenylphosphoranylidenepyruvic Acid p-*Chlorobenzoylpyruvoylhydrazide* (**10d**). Yield 77%, mp. 205–206°C dec. IR (NaCl, cm^{-1}): 3305–3315 (CO$\underline{\mathrm{NH}}$), 1698, 1663 ($\underline{\mathrm{CO}}$NH), 1575–1585 (CO chelate, P$\cdots$C$\cdots$C$\cdots$O). ^{1}H NMR (DMSO-d$_6$, δ): 7.15–7.80 (m, 20H, 3Ph, C_6H_4, P=$\underline{\mathrm{CH}}$). Anal. Calcd. for: $C_{31}H_{24}ClN_2O_5P$: C, 65.21; H, 4.24; N, 4.91; Found: C, 65.39; H, 4.03; N, 4.74.

Reaction of Triphenylphosphoranylidenepyruvic Acid Benzoylpyruvoylhydrazide (**10a**) *with Hydrazine Hydrate.* A mixture of the compound (**10a**) (0.54 g, 1 mmol) and 70% hydrazine (0.2 ml) in ethanol (30 ml) was heated up to reflux until the solid dissolved (1–2 min). After cooling to room temperature, the precipitate was collected and crystallized from toluene to give the ylide (**13**), yield 0.40 g (75%), mp. 264–265°C dec. IR (NaCl, cm^{-1}): 3280–3310 (CO$\underline{\mathrm{NH}}$), 1654, ($\underline{\mathrm{CO}}$NH), 1590–1610 (P$\cdots$C$\cdots$C$\cdots$O, C=C, Ph). ^{1}H NMR (DMSO-d$_6$, δ): 7.10–7.85 (m, 23H, 4Ph, CH cycle, P=$\underline{\mathrm{CH}}$), 9.85 (broad, 2H, 2$\underline{\mathrm{NH}}$CO), 13.60 (broad, 1H, NH cycle). Anal. Calcd. for: $C_{31}H_{25}N_4O_3P$: C, 69.92; H, 4.73; N, 10.52; Found: C, 70.13; H, 4.85; N, 10.38.

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