β-Diphenylphosphorylated alkanones and related compounds: synthesis and structure*

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The reactions of diphenyl(diisopropyl)chlorophosphine with arylidene(heteroarylidene)-acetones and 3-benzylidenepentane-2,4-dione in the presence of acetic acid proceed at a high rate at room temperature to afford the corresponding β-diorganylphosphorylated alkanones and alkanediones in high yields. The reaction of diphenylchlorophosphine with 4-methoxybut-3-en-2-one and dibenzylideneacetone carried out under similar conditions at the equimolar reagent ratio can serve as a convenient method for the synthesis of unique β-diphenylphosphoryl-alkenones. The structures of compounds obtained were established by IR, Raman, and NMR spectroscopy and X-ray diffraction.

Key words: ylidene alkanones (alkanediones), chlorophosphines, β-diorganylphosphoryl-alkanones (alkenones/alkanediones), synthesis, IR, Raman, NMR spectra, X-ray diffraction study.

β-Diphenylphosphorylated alkanones are known since the first half of XX century; however, this type of functionalized organophosphorus compounds became of special interest only in recent times. For example, by the example of 4-methyl-4-(diphenylphosphoryl)pentan-2-one, it was demonstrated that such ketones can act as fire retarders for polyvinyl chloride[1] and agents for extraction of actinides and lanthanides.[2] In addition, β-diphenylphosphorylated alkanones can be used as precursors for the preparation of original phosphoryl-containing heterocycles, e.g., 1,8- and 1,6-naphthyridines.[3,4] A special interest for the phosphoryl ketones containing the P(O)—C—C—C(O) fragment is caused by their high thermal stability,[5] which favorably distinguishes such organophosphorus compounds from the analogous sulfoxides,[6] selenoxides,[7] and amine oxides.[8]

It should be noted that the necessary condition for successful application of β-diphenylphosphorylated alkanones is the design of simple, efficient, and readily producible methods for the syntheis of these compounds. The organophosphorus ketones of the above-mentioned type have been obtained for the first time in 1923 by J. Conant in the reaction of diphenylchlorophosphine (DPCP) with chalcones in glacial acetic acid[9] in suficiently high yields (77—85%). Later, this approach named as the Conant reaction was applied for the syntheses of a number of other β-diphenylphosphoryl alkanones based on aliphatic α,β-enones, although the yields of target compounds were much lower than in the case of chalcones to be 66—72%.[10] The characteristic of these reactions is sufficiently hard reaction conditions, namely, refluxing in acetic acid acting as a solvent. The use of acetonitrile instead of acetic acid in the reaction of DPCP with pent-3-en-2-one resulted in a noticeable decrease in the process efficiency: the yield of the corresponding phosphoryl ketone decreased from 66% to 53%.[10] Later, a significantly softer and efficient variant of the Conant reaction has been proposed, which showed that the reaction of DPCP and simplest α,β-enone, *viz.*, methyl vinyl ketone, in the presence of glacial acetic acid (the reagent ratio was 1 : 1.1 : 1.1) in dry benzene proceeds quite vigorously even at room temperature[11] to form 4-(diphenylphosphoryl)butan-2-one (**1**)** in virtually quantitative yield. The change in the way of isolation of the target product in this procedure allowed first preparation of phosphoryl ketone **1** in the crystalline state by preserving a very high yield (91%).[3]

Unfortunately, to date only one representative of β-diphenylphosphorylated alkanones, *viz.*, compound **1**, was obtained by such modified Conant reaction; for this reason, the question on the possibility of a wider application of this promising synthetic method is still open.

* Dedicated to the Academician of the Russian Academy of Sciences I. P. Beletskaya on occassion of her anniversary.

† Deceased.

** In Ref. 11, phosphoryl ketone **1** was isolated as an oil.

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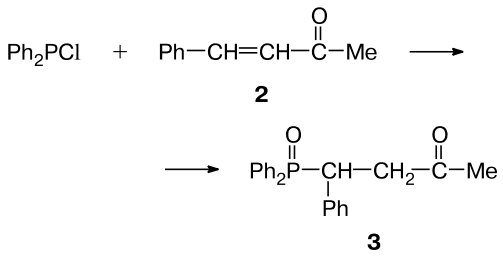
Results and Discussion

The aim of the present work was to study whether it is possible to apply the modified Conant reaction for the preparation of other representatives of β-diphenylphosphorylalkanones, as well as their related compounds, in particular, β-diphenylphosphorylated alkenones and alkanediones.

Various 4-aryl(hetaryl)substituted but-3-en-2-ones were selected first of all as the starting α,β-enones. It is known that these enones are problematic to use for the synthesis of the corresponding phosphorylketones by the reaction with hydrophosphoryl compounds, since, according to the literature data, under normal conditions diaryl(dialkyl)phosphinous acids do not add at all to these enones (provided that the starting acids are purified thoroughly[12]) or the addition proceeds not at the C=C*, but at the C=O bond.[13] The fact that these enones are commercially available or can be synthesized readily from the corresponding aldehyde or acetone can be referred to their advantages, which seems to be important from the viewpoint of practical application of β-phosphorylated alkanones prepared from them.

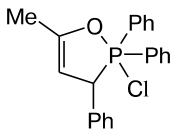
$^{31}P\{^{1}H\}$ NMR spectral monitoring showed that the reaction of *trans*-4-phenylbut-3-en-2-one (**2**) with DPCP in the presence of glacial acetic acid at room temperature proceeds at a sufficiently high rate to form 4-(diphenylphosphoryl)-4-phenylbutan-2-one (**3**).** It should be noted that, under these conditions, no formation of side products in any noticeable amounts was observed (Scheme 1), thanks to which we succeeded in isolation of the analytically pure phosphorylketone **3** in a very high yield (89.7%).

Scheme 1



Reagents and conditions: AcOH, ~20 °C, benzene.

Irrespective of the reaction time, the ^{31}P NMR spectra of the reaction mixture display nor signals for diphenylphosphinous acid, which was initially postulated as the Conant reaction intermediate,[10,15] nor signals in the region typical of semiproduct **4** containing the pentacoordinated phosphorus atom whose analog (δ −4.5) has been observed earlier when studying the reaction mechanism of DPCP with methyl vinyl ketone.[11]



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To elucidate the reaction mechanism of DPCP with enone **2**, we performed the test experiment consisting in the reaction of these reagents in benzene in the absence of acetic acid at room temperature. The $^{31}P\{^{1}H\}$ NMR spectrum of the above-mentioned reaction mixture recorded after 1 h displays an intensive (29%) singlet signal at δ −7.91, which more likely belongs to product **4**. The intensity of this signal increased slowly and reached the value of 47% 4 h after initiation of the reaction. When glacial acetic acid was added to the reaction mixture, the above-mentioned signal disappeared immediately and a signal having almost equal intensity appeared, which is typical of phosphoryl ketone **3**. It should be noted that, in this test experiment, we failed to detect diphenylphosphinous acid in the reaction mixture. The data obtained allow conclusion of that proceeding of the reaction of DPCP with α,β-enones through the intermediate formation step of the corresponding phosphoranes is general in character.

The composition of phosphoryl ketone **3** was confirmed by elemental analysis and its structure was confirmed by the IR and ^{1}H, $^{1}H\{^{31}P\}$, $^{13}C\{^{1}H\}$, $^{31}P\{^{1}H\}$ NMR spectral data. In particular, $^{31}P\{^{1}H\}$ NMR spectrum of this compound in deuterated chloroform displays a singlet signal at δ 33.62, *i.e.*, virtually in the same region where the corresponding signal of the simplest β-diphenylphosphorylated alkanone **1** (see Refs 3 and 11) appears. In the ^{1}H NMR spectrum of compound **3**, one can pay attention to the fact that the signal for the methylene protons is not a primary spectrum, but a quite composite multiplet. In the $^{1}H\{^{31}P\}$ spectrum (*i.e.*, recorded using broad-band signal suppression of spin-spin coupling between the protons and ^{31}P nuclei), there occurs the corresponding decrease in the multiplicity of this signal. The resulted data taken together allow interpretation of the signal for the CH_2 protons of ketone **3** as the AB part of the ABMX system (M and X are the ^{1}H and ^{31}P atomic nuclei of the >P(O)CH group, respectively) in the case of ^{1}H NMR spectra or ABM system in the case of $^{1}H\{^{31}P\}$ NMR spectra. This is observed due to the fact that the molecules of this ketone contain the asymmetric carbon atom being a part of the $Ph_2P(O)CHPh$ fragment; as a result, according to the prochirality concept,[16,17] the carbon atom of the neighbor methylene fragment is prochiral and the hydrogen atoms of this fragment are diastereotopic. It should be noted that

* In Ref. 14, the addition of diphenylphosphinous acid at the C=C bond of benzylideneacetone was shown to proceed only upon photolysis of the reaction mixture ($h\nu$ = 300 nm).

** The amount of unreacted DPCP after 2 h is 23%, only 3% of DPCP remains in the mixture after one day, and the reaction is completed after two days (according to the $^{31}P\{^{1}H\}$ NMR spectral data, the yield of compound **3** is 94%).

since the molecule of phosphorylated ketone **3** contains additional prochiral center, *viz.*, the phosphorus atom, the phenyl groups linked with this center must be diastereotopic as well. This is manifested in both the $^1H—^1H\{^{31}P\}$ and $^{13}C\{^1H\}$ NMR spectra where duplication of the signals for the carbon atoms of P-aromatic rings (*o*, *m*, *p*, and *ipso*) occurs. In the $^{13}C\{^1H\}$ NMR spectrum of the phosphorus-containing ketone **3**, the signal for the carbonyl carbon atom appears as a doublet ($^3J_{C,P}$ = 12.2 Hz), which suggests the *trans*-disposition of the C=O and P=O groups.[5]

The drawn conclusion is confirmed by the quantum chemical calculation, according to which the molecule of phosphoryl ketone **3** in the global minimum has antiperiplanar disposition of the C=O and P=O groups (Fig. 1).

The normal mode analysis of molecule **3** in this conformation showed that the P=O stretching vibration is mixed with the P—C and C—C vibrations and out-of-plane CH deformational vibrations of the phenyl rings and makes one or another contribution to several frequencies of normal modes in the range of 1100—1200 cm^{-1}, due to which the P=O stretching vibration in the IR spectra of diphenylphosphoryl compounds can have several absorption maxima. In particular, in the spectrum of solid phosphoryl ketone **3**, the P=O vibration was attributed to the intensive splitted band with the maxima at 1185 and 1177 cm^{-1}.

The C=O stretching vibration with the calculated frequency of 1716 cm^{-1} is fully characteristic and observed in the IR spectrum at 1717 cm^{-1}. The P=O and C=O stretching frequencies of compound **3** are typical of phosphoryl compounds with the phenyl substituents and of methyl ketones.[18]

In the IR spectrum of a solution of compound **3** in deuterated chloroform, the absorption maxima at 1184 and 1170 cm^{-1} are attributed to the P=O stretching vibration (the P=O group forms the hydrogen bond with the solvent, which is also evidenced by the shifted CD band of chloroform) and an high-intensity band at 1719 cm^{-1} belongs to the C=O stretching vibration.

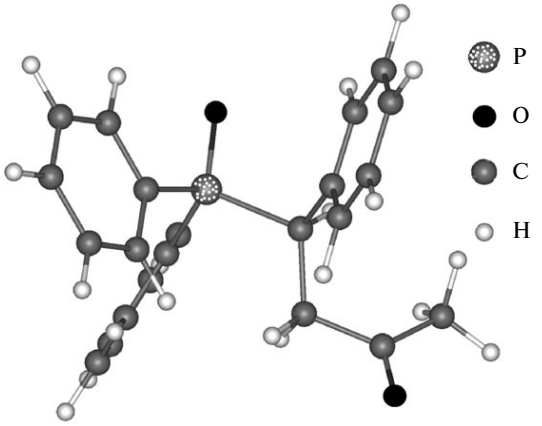
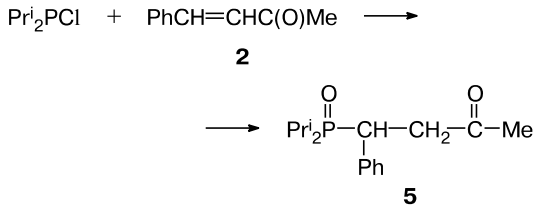


Fig. 1. Molecular conformation of **3** corresponding to the global minimum on the potential energy surface of the system.

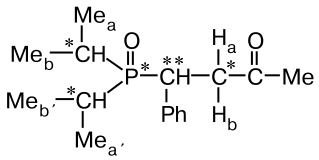
By the example of the reaction of diisopropylchlorophosphine Pr^i_2PCl with *trans*-4-phenylbut-3-en-2-one (**2**) which afforded 4-(diisopropylphosphoryl)-4-phenylbutan-2-one (**5**) in a sufficiently high yield, we showed that the modified Conant reaction can be a convenient method for the synthesis of alkanones containing not only diaryl, but also dialkylphosphoryl substituents (Scheme 2).

Scheme 2



Reagents and conditions: AcOH, ~20 °C, benzene.

The structure of phosphorylketone **5** was confirmed by IR, ^1H, $^1H\{^{31}P\}$, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectral data. The $^{31}P\{^1H\}$ NMR spectrum of this compound in chloroform contains a singlet signal at 56.85, *i.e.*, replacement of both phenyl groups at the phosphorus atom of diphenylphosphoryl ketone **3** with the isopropyl ones results in a considerable (by more than 20 ppm) down-field shift. The ^1H and ^{13}C NMR spectral patterns are significantly influenced by the presence of asymmetric carbon atom in the molecule of ketone **5**, as a result of which not only the phosphorus atom and the carbon atom of the CH_2 fragment (as in phosphoryl ketone **3**), but also both the α-carbon atoms of isopropyl substituents become prochiral.*



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In this case, both the isoropyl group themselves and the CH_3 substituents in each of these groups are diastereotopic, *i.e.*, there emerge necessary conditions for appearance of the so called "double magnetic non-equivalence" in the corresponding NMR spectra.[19] Indeed, the ^1H NMR spectrum of phosphoryl ketone **5** in deuterated chloroform in the corresponding regions displays two multiplets (doublets of septets) for the methyne protons and four doublets of doublets belonging to the methyl protons of these radicals. In the ^1H NMR spectrum of ketone **5**

* The prochiral centers are marked with an asterisk and the asymmetric site is marked with two asterisks.

recorded using the broad-band suppression of spin-spin coupling between protons and ^{31}P nuclei, these multiplets transform to two septet and four doublet signals, respectively.

Similarly, the effect of double magnetic non-equivalence manifests itself also in the $^{13}C\{^1H\}$ NMR spectrum of compound **5**, where two doublets belonging to the anisochronous α-carbon atoms of isopropyl radicals and four doublet signals for the carbon atoms of the magnetically non-equivalent methyl groups of these radicals are observed.

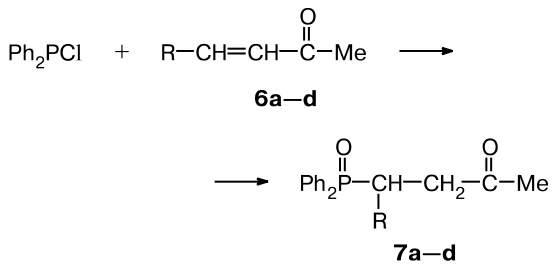
Thus, phosphoryl ketone **5** relates to a rare type of objects where the system of prochiral centers defining the existence of the double magnetic non-equivalence phenomenon in NMR spectra includes not only the carbon atoms (as is typically the case[19—21]), but also the pentavalent four-coordinated phosphorus atom.*

In the IR spectrum of solid compound **5**, the absorption bands at 1179 and 1166 cm^{-1} are related to the P=O stretching vibration and the band at 1721 cm^{-1} corresponds to the C=O vibration.

While studying the properties of diisopropylphosphoryl ketone **5**, we found that this compound possesses noticeable hygroscopicity, which, of certainly, will create problems upon its practical application. Since the probability of that other representatives of dialkylphosphoryl-containing alkanones will be found to be hygroscopic was high, the subsequent works on the design of diorganyl-phosphorylated ketones based on the modified Conant reaction were focused on the design of synthetic methods exclusively for the P,P-diphenyl derivatives.

We found that, under these reaction conditions, the reactions of DPCP with a number of 4-aryl- and 4-heteroarylbut-3-en-2-ones **6a—d** afford in a sufficiently high yield the corresponding 4-substituted 4-(diphenylphosphoryl)butan-2-ones **7a—d** (Scheme 3).

Scheme 3



R = *p*-$MeOC_6H_4$ (**a**), *p*-ClC_6H_4 (**b**), 2-thienyl (**c**), and 2-furyl (**d**)

Reagents and conditions: AcOH, ~20 °C, benzene.

The compounds obtained are air-stable white crystalline substances melting without decomposition. Their structures were confirmed by the IR and ^1H, $^1H\{^{31}P\}$, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectral data. In particular, by the analogy with the 4-phenyl substituted phosphoryl ketone **3**, the NMR spectra of compounds **7a—d** display anisochronicity of both the magnetically non-equivalent protons of the methylene groups and the protons and carbon atomic nuclei* of the P-aromatic rings. In the $^{13}C\{^1H\}$ NMR spectra of phosphorylated alkanones **7a—d**, as in the case of phosphoryl ketone **3**, the signals for the carbon atoms of C=O groups appear as doublets with $^3J_{C,P}$ = 12.1—13.3 Hz. The data obtained suggest that the anti-periplanar disposition the C=O and P=O groups in a series of β-diorganylphosphoryl alkanones is quite general in character.

The P=O stretching frequencies in the 4-aryl substituted phosphoryl ketones **7a** (1187 and 1175 cm^{-1}) and **7b** (1185 and 1175 cm^{-1}) are close to the corresponding frequencies for the 4-phenyl substituted ketone **3**. The C=O stretching vibrations of ketones **7a** and **7b** are observed at 1706 and 1715 cm^{-1}, respectively.

The IR spectrum of the thienyl derivative **7c** contains an intensive splitted band with the maximum at 1197 cm^{-1} and a shoulder at 1185 cm^{-1} and the spectrum of the furyl derivative **7d** contains the band at 1203 cm^{-1} with a shoulder at 1190 cm^{-1}. The high-frequency shift of the bands of compounds **7c** and **7d**, which can be assigned to the vibrations of the phosphoryl group, as compared to the aryl substituted compounds **7a** and **7b** can be explained by mixing of the P=O vibration with the vibrations of the thienyl and furyl rings, as well as by overlapping of the corresponding bands.** The C=O stretching vibration in compounds **7c** and **7d** has frequencies of 1709 and 1714 cm^{-1}, respectively.

Besides the spectral data, the structure of phosphoryl ketone **7c** was confirmed by the X-ray diffraction study (Fig. 2) of its crystalline solvate with chloroform. The geometry of the target molecule is characterized by the *trans* disposition of the C=O and P=O groups (the corresponding pseudo-torsion angle is 164.5(2)°). At the same time, the P=O group is in the *cis*-position relative to the C(16)—S bond of the thienyl substituent with the O(1)P(1)C(16)S(1) angle equal to 29.1(2)°. The main bond lengths fall within the value range typical of similar compounds. In the molecular crystal of the product, there are relatively weak contacts C—H···O, C—H···S, and

* The double magnetic nonequivalence in the NMR spectra of the system containing the prochiral phosphorus atom has been noted first in Ref. 22.

* For compounds **7a—c**, this effect appears for all four carbon nuclei (*o*, *m*, *p*, and *ipso*) of the corresponding groups and, for the furyl derivative **7d**, it appears only for three carbon nuclei (*m*, *p,* and *ipso*).

** For example, in particular, the IR spectra of the starting ylideneacetones **6c** and **6d** displayed the absorption bands at 1200 and 1202 cm^{-1}, respectively.

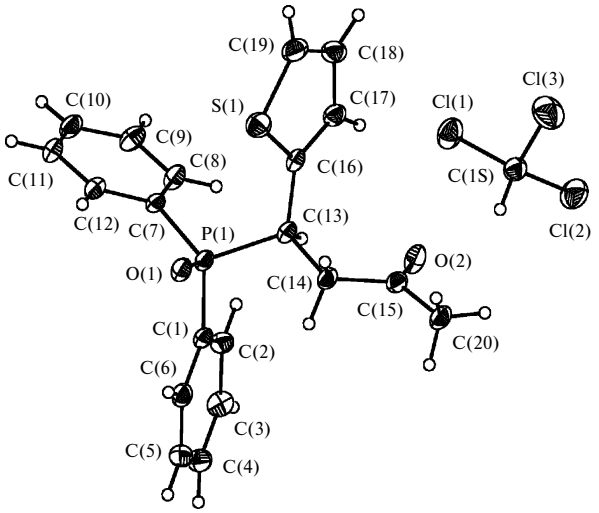
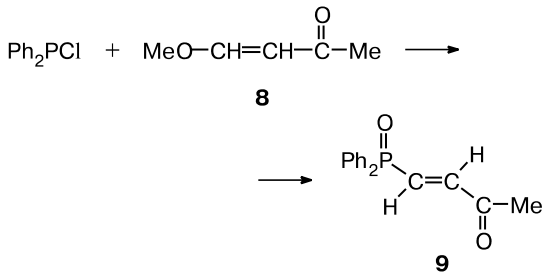


Fig. 2. Molecular structure of compound **7c** (as a solvate with chloroform). Non-hydrogen atoms are shown as thermal ellipsoids (p = 50%).

C—H···π-type with the shortest distances C···O, C···S, and C···C equal to 3.301(3), 3.826(3), and 3.651(3) Å, respectively. The solvate molecules of chloroform are retained in the crystal due to the C—H···O, C—H···Cl, and Cl···π contacts: the corresponding interatomic distances C···O, C···Cl, and Cl···C are 3.082(3), 3.563(3), and 3.418(3) Å.

Unexpectedly, we found that, under the modified Conant reaction conditions, the reaction between DPCP and 4-methoxybut-3-en-2-one (**8**) proceeds in such a way that the α,β-enone fragment is retained and the methoxy group is replaced with the diphenylphosphoryl radical, as a result of which (*E*)-4-(diphenylphosphoryl)but-3-en-2-one (**9**) forms (Scheme 4). Thus, this reaction is not only a convenient method for the syntheses of various β-diorganylphosphorylated alkanones, but also a novel simple approach to the preparation of the hardly available corresponding phosphorylated alkenones. Earlier, this compound has been obtained from DPCP by the complex four-step process in a yield of only ~15%.[23]

Scheme 4



Reagents and conditions: AcOH, ~20 °C, benzene.

The structure of compound **9** was confirmed by the IR and NMR spectral data.

In the compounds containing the C=O and C=C double bonds, the stretching frequencies of these bonds decrease due to the conjugation: the stretching frequency of the C=O bond is typically 1685—1665 cm^{-1} and that of the C=C bond is about 1600 cm^{-1} (see Ref. 18). The IR spectrum of the starting reagent **8** displays two pairs of bands belonging to the C=O and C=C vibrations: 1690 (C=O) and 1598 (C=C); 1650 (C=O) and 1620 (C=C) cm^{-1} which likely correspond to two conformers with different degrees of double-bond conjugation and mixing of their vibrations. The IR spectrum of the phosphoryl-substituted ketone **9** displays a high-intensity band at 1693 cm^{-1} with a shoulder at 1701 cm^{-1} and a rather weak band at 1604 cm^{-1}. In the Raman spectrum, the corresponding splitted line is low-intensity and the line at 1606 cm^{-1} is more intensive. This allows assignment of the high-frequency splitted line (band) to the C=O vibration and the low-frequency one to the C=C vibration. As was said, the analogous bands were observed in the spectrum of one of the conformers of the starting compound **8**. It appears that, in the molecule of **9**, only one of the possible disposition of the C=C and C=O groups is stabilized. The phosphoryl vibration appears in the IR spectrum of the solid sample of **9** as a high-intensity absorption band at 1185 cm^{-1}.

In the ^1H NMR spectra of phosphoryl alkenone **9**, the value of spin-spin coupling constant between the protons of the —CH=CH— fragment ($^3J_{H,H} \approx 17$ Hz) suggests the *trans*-configuration of this fragment, which was confirmed by the X-ray diffraction study (Fig. 3). According to the data obtained, compound **9** crystallizes with two independent molecules in the unit cell having close values of all geometric parameters. In particular, the pseudo-torsion

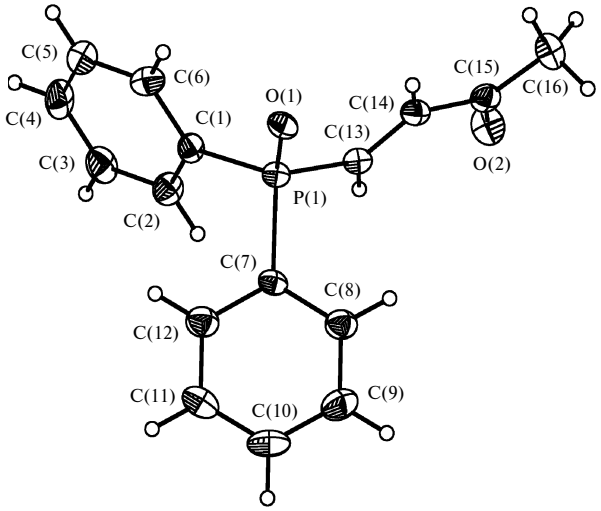
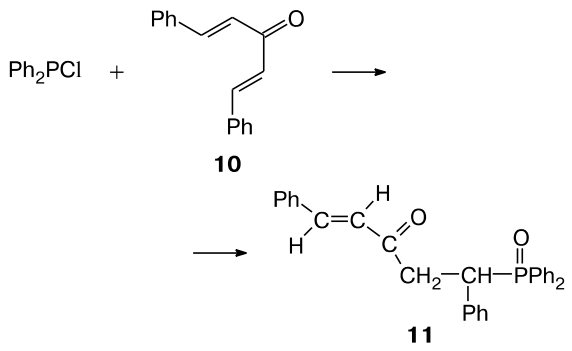


Fig. 3. Molecular structure of compound **9**. Non-hydrogen atoms are shown as thermal ellipsoids (p = 50%).

angle between the P=O and C=O groups is 172.5(1) and 169.7(1)°. The molecules in the crystal form infinite chains on a rota basis through sufficiently strong C—H···O bonds with the shortest distance C···O equal to 3.098(3) Å, the corresponding CHO angle reaching 154.0(1)°. The resulted associates are further stabilized through the C—H···π-contacts (C···C 3.696(3) Å) and combined with each other to form the three-dimensional framework by means of many weaker contacts of the C—H···O, C—H···π, π···π, and H···H type.

By the reaction of DPCP and dienones containing the —CH=CH—C(O)—CH=CH— fragment under the modified Conant conditions, unique hybrid β-diphenylphosphorylated ketones can be synthesized, where the carbon atom of the carbonyl group is linked simultaneously with both the alkane and alkene fragmetns. For example, (*E*)-5-(diphenylphosphoryl)-1,5-diphenylpent-1-en-3-one (**11**) was obtained in a high yield starting from DPCP and *trans*,*trans*-dibenzylideneacetone (**10**) (Scheme 5).

Scheme 5



Reagents and conditions: AcOH, ~20 °C, benzene.

In the IR spectrum of compound **11**, the absorption bands at 1186 and 1174 cm^{-1} correspond to the P=O vibration. In the region of C=O and C=C stretching vibrations, the band at 1649 cm^{-1} has highest intensity and the bands at 1690, 1625, and 1615 cm^{-1} have medium intensities. In the Raman spectrum, the lines at 1627 and 1599 cm^{-1} are intensive. The band at 1651 cm^{-1} with a shoulder at about 1700 cm^{-1} is considerably weaker. This allows interpretation of the bands at about 1700 and 1650 cm^{-1} as those corresponding to the C=O stretching vibration and the bands at about 1625 and 1600 cm^{-1} as those corresponding to the C=C stretching vibration in two conformers. The analogous absorption bands were observed for the starting dienone **10** (and the above-mentioned α,β-enone **8**). Thus, in contrast to phosphorylenone **9**, if the C=C bond in the molecule of **11** is in the terminal position, this phosphoryl alkenone **11** can exist as different conformers differing in the mutual arrangement of the C=O and C=C groups.

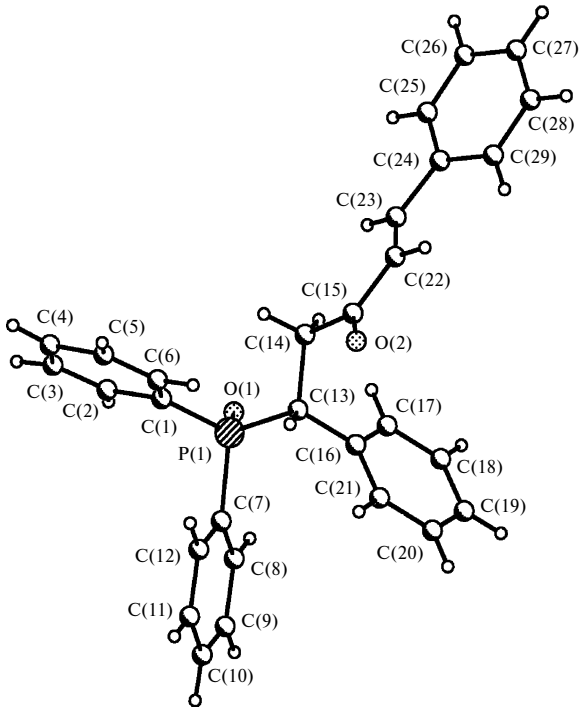


Fig. 4. Molecular structure of compound **11**. Non-hydrogen atoms are shown as thermal ellipsoids (p = 50%).

The resulted compound **11** remains the *trans*-configuration of the carbon-carbon double bond, which was confirmed by X-ray diffraction (Fig. 4). In particular, the torsion angle C(15)C(22)C(23)C(24) is 179.0(1)°. The P=O and C=O groups are in the *trans*-position relative to each other with the corresponding pseudo-torsion angle of 166.8(1)°. The phenyl substituent at the C(13) atom is positioned in the molecule such that that the torsion angles O(1)P(1)C(13)C(16) and O(2)C(15)C(13)C(16) are equal to 64.8(1) and 90.8(1)°, respectively. In the crystal, the molecules are retained through many weak C—H···O and C—H···π contacts among which one can point out C—H···O (the distance C···O from 3.320(2) Å) involving both the C=O and P=O groups, which combine the molecules into infinite chains.

We found that the modified Conant reaction can be applied successfully not only for the synthesis of various β-diphenylphosphorylated alkan- and alkenones, but also for the preparation of the corresponding of phosphorus-containing alkanediones. For example, the reaction of DPCP with 3-benzylidenepentan-2,4-dione (**12**) in the presence of acetic acid affords 3-[α-(diphenylphosphoryl)-benzyl]pentan-2,4-dione (**13**) in a high yield (Scheme 6). Earlier, this compound has been isolated in a very low yield upon action of dry HCl on the adduct of **12** and $MeOPPh_2$.[24]

In the molecule of phosphoryl ketone **13**, there are two methyne atoms: the assymetric one being a part of the

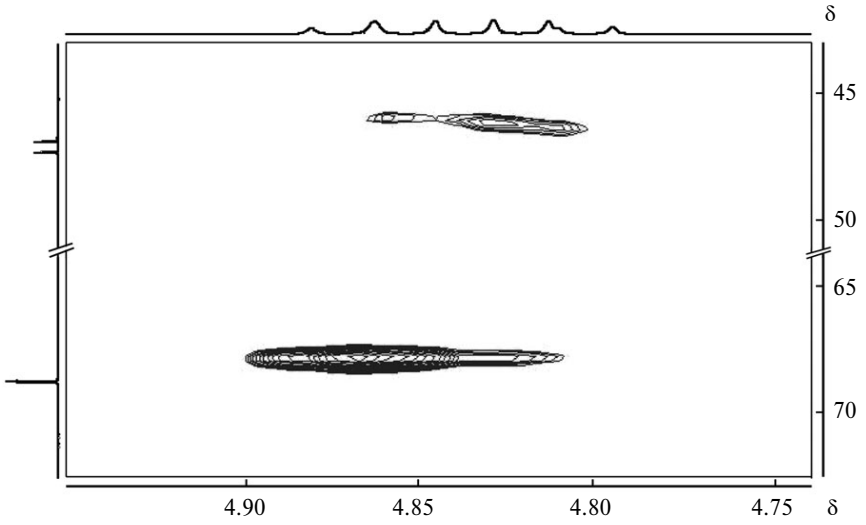
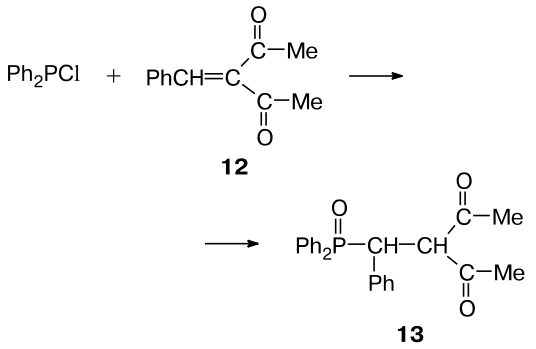


Fig. 5. $^{1}H—^{13}C$ NMR spectrum of compound **13**.

Scheme 6



Reagents and conditions: AcOH, ~20 °C, benzene.

P(O)CH fragment and the prochiral one being a part of the $CH(COCH_3)_2$ fragment. For this reason, the $COCH_3$ radicals are diastereotopic and magnetically nonequivalent in the achiral medium, which is manifested in the $^{1}H—^{1}H\{^{31}P\}$ and $^{13}C\{^{1}H\}$ NMR spectra as duplication of the signals for the corresponding tracer nuclei. In addition, the phosphorus atom is also prochiral, as a result of which the $^{13}C\{^{1}H\}$ NMR spectrum displays duplication of the signals for the carbon atoms of diastereotopic phenyl groups as in the case of stereochemically similar phosphoryl monoketone **3**.

To assign the closely adjacent signals for the methyne protons of the CHP(O) and $CH(COCH_3)_2$ groups in the ^{1}H NMR spectrum, we used the corresponding $^{1}H—^{13}C$ correlation (HMQC) (Fig. 5).

Calculation of the molecular conformation of **13** (Fig. 6) showed that, in the global minimum, the C=O bonds are almost parallel to each other and, therefore, the C=O vibrations are related as in-phase and antiphase ones and have frequencies of 1690 cm^{-1} and 1721 cm^{-1}, respectively, according to the normal-mode calculation.

The IR spectrum of the solid sample of **13** displays a strong absorption band at 1703 cm^{-1} and medium-intensity band at 1724 cm^{-1} corresponding to the in-phase and antiphase C=O stretching vibrations, respectively, and confirming the molecular conformation with the parallelly oriented C=O bonds.

It is interesting that the spectrum of a solution of this compound in $CDCl_3$ displays three carbonyl vibration bands: at 1700 (very strong) and 1724 (medium) cm^{-1}, which by analogy can be attributed to the antiphase and inphase vibrations of the molecule having conformation with the parallel C=O bonds, and at 1736 cm^{-1}, which suggests the presence of another conformation in solution where the C=O stretching vibrations do not interact as the inphase and antiphase ones and, therefore, these bonds are not parallel.

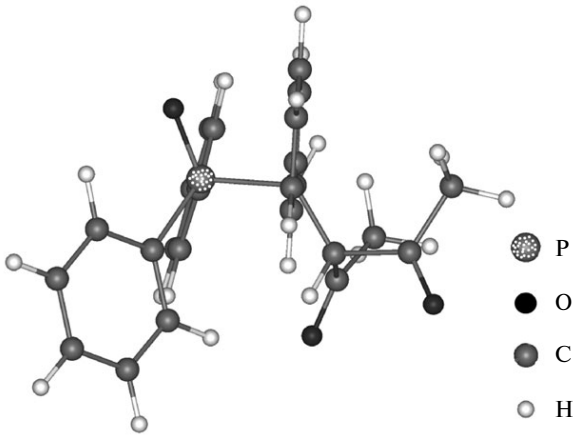


Fig. 6. Molecular conformation of **13** corresponding to the global minimum on on the potential energy surface of the system.

An intensive band at 1177 cm^{-1} with a shoulder at 1165 cm^{-1} corresponds to the P=O stretching vibration. In the spectrum of solution ($CDCl_3$), the corresponding band with a low-frequency shoulder is observed at 1184 cm^{-1}.

Thus, the reaction of diaryl(dialkyl)chlorophosphines with α,β-enones, dienones, and endiones in the presence of acetic acid in benzene at room temperature is a simple and efficient method for the syntheses of various β-diorganylphosphorylated alkanones, alkenones, and alkanediones. According to the preliminary experimental data, the corresponding phosphoryl-containing carbonyl compounds can efficiently extract actinides and lanthanides from the nitric-acid media,[25] which evidences a promising future of further studies in this line of research.

Experimental

The ^1H, $^1H\{^{31}P\}$, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra of synthesized compounds were recorded on Bruker AV-400 (400.13 MHz (^1H and $^1H\{^{31}P\}$), 100.61 ($^{13}C\{^1H\}$), and 161.98 MHz ($^{31}P\{^1H\}$)) and Bruker AV-600 (600.22 MHz (^1H) and 150.925 MHz (^{13}C)) instruments in $CDCl_3$, the solution concentration was 0.1 mol L^{-1}. The signals for residual protons and carbon nuclei of deuterated solvent served as the internal standards for ^1H, $^1H\{^{31}P\}$, and $^{13}C\{^1H\}$ NMR spectra, respectively, and 85% H_3PO_4 served as the external standard for $^{31}P\{^1H\}$ NMR spectra.

IR spectra were obtained on a Bruker Tensor 37 FT-IR spectrometer. Raman spectra were recorded on a Jobin-Yvon LabRam 300 spectrometer equipped with a microscope and laser CCD detector. The He-Ne laser line with a wavelength of 632.8 nm and power no more than 10 mW was used as the exciting line.

Single crystals of β-diphenylphosphorylated alkan- and alkenones **7c**, **9**, and **11** suitable for the X-ray diffraction study were obtained by isothermal evaporation of solutions of the corresponding compounds in chloroform at room temperature. X-ray diffraction studies were performed on a SMART APEX 1000 CCD diffractometer (Mo-Kα radiation, graphite monochromator, ω-scanning). The structures were solved by the direct method and refined by the least-squares method in the anisotropic full-matrix approximation over F^2_{hkl}. The hydrogen atomic positions were calculated geometrically and refined in the isotropic approximation by the riding model. The main crystallographic data and refinement parameters are given in Table 1. All calculations were performed using the SHELXTL PLUS program package.

Quantum chemical calculations were performed in terms of Density Functional Theory (DFT) by the Priroda 6 program package (2006.08.20)[26,27] using the PBE functional.[28] Optimization of geometric parameters and calculation of normal-mode frequencies and intensities for the conformation in the region of global minimum were performed using the basis4 relativistic basis set.

The starting α,β-enones **2**, **6c**,**d**, and **8** and dienone **10** (Acros), as well as endione **12** (Aldrich) were used without addi-

Table 1. Main crystallographic data and X-ray diffraction parameters for compounds **7c**, **9**, and **11**

Parameter	**7c**	**9**	**11**
Molecular formula	$C_{21}H_{20}Cl_3O_2PS$	$C_{16}H_{15}O_2P$	$C_{29}H_{25}O_2P$
Molecular weight	473.75	270.25	436.46
T/K	120	120	120
Crystal system	Rhombic	Monoclinic	Monoclinic
Space group	*Pbca*	$P2_1/c$	$C2$
Z	8	8	4
a/Å	8.9917(8)	10.7132(18)	19.1178(12)
b/Å	20.8818(19)	16.441(2)	5.6357(3)
c/Å	23.220(2)	15.829(2)	21.7194(13)
α/deg	90.00	90.00	90.00
β/deg	90.00	93.165(18)	108.1140(10)
γ/deg	90.00	90.00	90.00
V/Å^3	4359.9(7)	2783.8(7)	2224.1(2)
d_{calc}/g cm^{-3}	1.443	1.290	1.303
μ/cm^{-1}	6.05	1.92	1.48
F(000)	1952	1136	920
$2\theta_{max}$/deg	58	56	58
Number of reflections measured	45279	15572	12429
Number of independent reflections	5792	6663	5911
Number of reflections with $I > 2\sigma(I)$	3840	3486	4747
Number of parameters refined	254	345	289
R_1	0.0496	0.0525	0.0480
wR_2	0.1301	0.1269	0.1084
GOOF	1.003	1.004	1.000
Residual electron density (ρ_{max}/ρ_{min})/e Å^{-3}	0.816/−0.594	0.635/−0.360	0.460/−0.241

tional purification. Enones **6a**,**b** were synthesized from the corresponding substituted benzaldehydes and acetone in the presence of catalytic amounts of morpholine trifluoroacetate according to a known procedure.[29] DPCP and diisopropylchlorophosphine (Acros) were purified by vacuum distillation just prior to the reaction. Glacial acetic acid (reagent grade) was distilled prior to the reaction. Benzene was dried prior to use by distillation over P_2O_5. Organic solvents were purified according to the standard procedures.[30] All operations with chlorophosphines were performed in the argon atmosphere. Elemental analysis was performed at the Laboratory of Microanalysis, INEOS RAS.

4-(Diphenylphosphoryl)-4-phenylbutan-2-one (3). To a solution of *trans*-4-phenylbut-3-en-2-one (**2**) (0.903 g, 6.18 mmol) in benzene (5 mL), a solution of DPCP (1.323 g, 6 mmol) in benzene (3 mL) and then a soltuion of glacial acetic acid (0.408 g, 6.8 mmol) in benzene (3 mL) were added dropwise with stirring. The reaction mixture was kept for 48 h at ~20 °C, the solvent and other volatile substances were removed *in vacuo*, and the residue was dissolved in chloroform (20 mL) and filtered through basic Al_2O_3 (2.5 g). Al_2O_3 was washed with chloroform (2×5 mL); the combined filtrates were evaporated to dryness, and a mixture of diethyl ether (5 mL) and hexane (10 mL) was added to the residue. The mixture was refluxed for 1 h and filtered off after cooling, washed on a filter with a mixture of diethyl ether (5 mL) and hexane (10 mL), and dried in air. The yield was 1.87 g (89.7%), m.p. 198—199 °C (*cf.* Ref. 15: m.p. 170 °C). Found (%): C, 76.03; H, 6.18; P, 8.87. $C_{22}H_{21}O_2P$. Calculated (%): C, 75.85; H, 6.08; P, 8.89. IR (KBr), ν/cm^{-1}: 1185, 1177 (P=O); 1717 (C=O). $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ: 33.62 (s). ^1H NMR (400 MHz, $CDCl_3$), δ: 1.93 (s, 3 H, CH_3); 2.92 (ddd, 1 H, $C\underline{H}_aH_b$, $^3J_{H_a,H}$ = = 2.8 Hz, $^3J_{H_a,P}$ = 11.2 Hz, $^2J_{H_a,H_b}$ = 17.9 Hz); 3.31 (ddd, 1 H, $CH_a\underline{H}_b$, $^3J_{H_b,H}$ = 10.2 Hz, $^3J_{H_b,P}$ = 5.3 Hz, $^2J_{H_b,H_a}$ = 17.8 Hz); 4.20 (ddd, 1 H, CHP, $^3J_{H,H_a}$ = 2.5 Hz, $^3J_{H,H_b}$ = 9.9 Hz, $^2J_{H,P}$ = = 7.3 Hz); 7.06—7.17 (m, 3 H, *m*- + *p*-C_6H_5C); 7.18—7.24 (m, 2 H, *m*-C_6H_5P); 7.25—7.35 (m, 3 H, *o*-C_6H_5C + *p*-C_6H_5P); 7.37—7.46 (m, 2 H, *o*-C_6H_5P); 7.47—7.58 (m, 3 H, *m*- + *p*-C_6H_5P); 7.86—7.97 (m, 2 H, *o*-C_6H_5P). $^1H\{^{31}P\}$ NMR ($CDCl_3$), δ: 1.93 (s, 3 H, CH_3); 2.93 (dd, 1 H, $C\underline{H}_aH_b$, $^3J_{H_a,H}$ = 2.4 Hz, $^2J_{H_a,H_b}$ = = 18.0 Hz); 3.31 (dd, 1 H, $CH_a\underline{H}_b$, $^3J_{H_b,H}$ = 10.1 Hz, $^2J_{H_b,H_a}$ = = 17.8 Hz); 4.20 (dd, 1 H, CHP, $^3J_{H,H_a}$ = 2.6 Hz, $^3J_{H,H_b}$ = = 10.0 Hz); 7.06—7.17 (m, 3 H, *m*- + *p*-C_6H_5C); 7.21 (t, 2 H, *m*-C_6H_5P, $^3J_{H,H}$ = 7.5 Hz); 7.24—7.35 (m, 3 H, *o*-C_6H_5C + + *p*-C_6H_5P); 7.42 (d, 2 H, *o*-C_6H_5P, $^3J_{H,H}$ = 7.9 Hz); 7.47—7.58 (m, 3 H, *m*- + *p*-C_6H_5P); 7.87—7.96 (m, 2 H, *o*-C_6H_5P). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$), δ: 30.62 (s, CH_3); 41.11 (d, CH, $^1J_{C,P}$ = 68.6 Hz); 43.57 (s, CH_2); 127.12 (d, *p*-C_6H_5C, $^5J_{C,P}$ = = 2.2 Hz); 128.07 (d, *m*-C_6H_5P, $^3J_{C,P}$ = 11.6 Hz); 128.35 (d, *m*-C_6H_5C, $^4J_{C,P}$ = 1.7 Hz); 128.89 (d, *m*-C_6H_5P, $^3J_{C,P}$ = = 11.6 Hz); 129.73 (d, *o*-C_6H_5C, $^3J_{C,P}$ = 5.5 Hz); 130.98 (d, *o*-C_6H_5P, $^2J_{C,P}$ = 8.8 Hz); 131.32 (d, *o*-C_6H_5P, $^2J_{C,P}$ = 8.8 Hz); 131.43 (d, *p*-C_6H_5P, $^4J_{C,P}$ = 2.8 Hz); 131.45 (d, *ipso*-C_6H_5P, $^1J_{C,P}$ = 94.5 Hz); 131.50 (d, *ipso*-C_6H_5P, $^1J_{C,P}$ = 100.6 Hz); 132.02 (d, *p*-C_6H_5P, $^4J_{C,P}$ = = 2.2 Hz); 135.86 (d, *ipso*-C_6H_5C, $^2J_{C,P}$ = 5.5 Hz); 205.35 (d, C=O, $^3J_{C,P}$ = 12.2 Hz).

4-(Diisopropylphosphoryl)-4-phenylbutan-2-one (5). To a solution of *trans*-4-phenylbut-3-en-2-one (**2**) (1.75 g, 12 mmol) in benzene (5 mL), a solution of diisopropylchlorophosphine (1.9 g, 12.45 mmol) in benzene (5 mL) and a solution of glacial acetic acid (0.79 g, 13.15 mmol) in benzene (10 mL) were added successively with stirring. The reaction mixture was kept for 72 h at ~20 °C, concentrated twice, and filtered through basic Al_2O_3 (4 g). Al_2O_3 was washed with benzene (2×5 mL), the combined filtrates were evaporated *in vacuo*, the residue was dissolved in the minimum amount of boiling hexane and kept for 12 h at −15 °C, and the precipitate that formed was separated, washed with cooled to 0 °C hexane (5 mL), and dried *in vacuo* (~10 Torr) for 1 h at ~20 °C. The yield was 2.36 g (70.1%), m.p. 72—73 °C. Found, (%): C, 68.42; H, 8.98; P, 11.09. $C_{16}H_{25}O_2P$. Calculated (%): C, 68.55; H, 8.99; P, 11.05. IR (KBr), ν/cm^{-1}: 1179, 1166 (P=O); 1721 (C=O). $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ: 56.85 (s). ^1H NMR (400 MHz, $CDCl_3$), δ: 0.85 (dd, 3 H, $C\underline{H}_3CH$, $^3J_{H,H}$ = = 7.3 Hz, $^3J_{H,P}$ = 15.2 Hz); 1.03 (dd, 3 H, $C\underline{H}_3CH$, $^3J_{H,H}$ = = 7.3 Hz, $^3J_{H,P}$ = 14.5 Hz); 1.24 (dd, 3 H, $C\underline{H}_3CH$, $^3J_{H,H}$ = 7.2 Hz, $^3J_{H,P}$ = 14.5 Hz); 1.25 (dd, 3 H, $C\underline{H}_3CH$, $^3J_{H,H}$ = 7.3 Hz, $^3J_{H,P}$ = 14.5 Hz); 1.80 (d.sept, 1 H, $CH_3C\underline{H}$, $^3J_{H,H}$ = 7.3 Hz, $^2J_{H,P}$ = 14.6 Hz); 2.02 (s, 3 H, $CH_3C(O)$), 2.15 (d.sept, 1 H, $CH_3C\underline{H}$, $^3J_{H,H}$ = 7.3 Hz, $^2J_{H,P}$ = 12.7 Hz); 3.11—3.25 (m, 2 H, CH_2); 3.82 (ddd, 1 H, CHP, $^3J_{H,H}$ = 4.2 Hz, $^3J_{H,H}$ = 8.7 Hz, $^2J_{H,P}$ = 8.7 Hz); 7.17—7.23 (m, 1 H, *p*-C_6H_5); 7.24—7.31 (m, 2 H, *m*-C_6H_5); 7.35—7.40 (m, 2 H, *o*-C_6H_5). $^1H\{^{31}P\}$ NMR ($CDCl_3$), δ: 0.85 (d, 3 H, $C\underline{H}_3CH$, $^3J_{H,H}$ = 7.3 Hz); 1.03 (d, 3 H, $C\underline{H}_3CH$, $^3J_{H,H}$ = 7.3 Hz); 1.24 (d, 3 H, $C\underline{H}_3CH$, $^3J_{H,H}$ = 7.2 Hz); 1.25 (d, 3 H, $C\underline{H}_3CH$, $^3J_{H,H}$ = 7.4 Hz); 1.80 (septet, 1 H, $CH_3C\underline{H}$, $^3J_{H,H}$ = 7.3 Hz); 2.02 (s, 3 H, $CH_3C(O)$), 2.14 (septet, 1 H, $CH_3C\underline{H}$, $^3J_{H,H}$ = 7.3 Hz); 3.16 (dd, 1 H, $C\underline{H}_aH_b$, $^3J_{H_a,H}$ = 4.3 Hz, $^2J_{H_a,H_b}$ = 17.9 Hz); 3.20 (dd, 1 H, $CH_a\underline{H}_b$, $^3J_{H_b,H}$ = 8.8 Hz, $^2J_{H_b,H_a}$ = 17.9 Hz); 3.82 (dd, 1 H, CHP, $^3J_{H,H_a}$ = 4.3 Hz, $^3J_{H,H_b}$ = 8.9 Hz); 7.17—7.23 (m, 1 H, *p*-C_6H_5); 7.24—7.30 (m, 2 H, *m*-C_6H_5); 7.35—7.40 (m, 2 H, *o*-C_6H_5). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$), δ: 16.06 (d, $\underline{C}H_3CH$, $^2J_{C,P}$ = 2.8); 16.37 (d, $\underline{C}H_3CH$, $^2J_{C,P}$ = 2.2 Hz); 16.76 (d, $\underline{C}H_3CH$, $^2J_{C,P}$ = 2.8 Hz); 17.10 (d, $\underline{C}H_3CH$, $^2J_{C,P}$ = 2.2 Hz); 26.09 (d, $CH_3\underline{C}H$, $^1J_{C,P}$ = = 63.6 Hz); 26.10 (d, $CH_3\underline{C}H$, $^1J_{C,P}$ = 59.7 Hz); 30.72 (s, $\underline{C}H_3C(O)$), 37.17 (d, CHP, $^1J_{C,P}$ = 56.4); 44.30 (d, CH_2, $^2J_{C,P}$ = 1.1 Hz); 127.26 (d, *p*-C_6H_5, $^5J_{C,P}$ = 2.2 Hz); 128.79 (d, *m*-C_6H_5, $^4J_{C,P}$ = 1.7 Hz); 129.28 (d, *o*-C_6H_5, $^3J_{C,P}$ = 5.0 Hz); 137.60 (d, *ipso*-C_6H_5, $^2J_{C,P}$ = 4.4 Hz); 205.64 (d, C=O, $^3J_{C,P}$ = = 10.5 Hz).

4-(Diphenylphosphoryl)-4-(*p*-methoxyphenyl)butan-2-one (7a). To a solution of 4-(*p*-methoxyphenyl)but-3-en-2-one (**6a**) (1.088 g, 6.18 mmol) in benzene (5 mL), DPCP (1.323 g, 6 mmol) and a solution of glacial acetic acid (0.408 g, 6.8 mmol) in benzene (3 mL) were added dropwise in succession. The reaction mixture was kept for 24 h at ~20 °C, treated analogously to the procedure for compound **3**, recrystallized from acetonitrile, and dried *in vacuo* (~1 Torr) for 2 h at 125 °C. The yield was 2.01 g (88.7%), m.p. 207.5—209.0 °C. Found (%): C, 73.00; H, 6.18; P, ...8.16. $C_{23}H_{23}O_3P$. Calculated (%): C, 73.00; H, 6.13; P, 8.19. IR (KBr), ν/cm^{-1}: 1187, 1175 (P=O); 1706 (C=O). $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ: 33.64 (s). ^1H NMR (400 MHz, $CDCl_3$), δ: 1.93 (s, 3 H, CH_3); 2.88 (ddd, 1 H, $C\underline{H}_aH_b$, $^3J_{H_a,H}$ = 2.8 Hz, $^3J_{H_a,P}$ = 10.8 Hz, $^2J_{H_a,H_b}$ = 17.9 Hz); 3.27 (ddd, 1 H, $CH_a\underline{H}_b$, $^3J_{H_b,H}$ = 10.4 Hz, $^3J_{H_b,P}$ = 5.2 Hz, $^2J_{Hb,H_a}$ = 17.8 Hz); 3.70 (s, 3 H, CH_3O); 4.15 (ddd, 1 H, CHP, $^3J_{H,H_a}$ = 2.9 Hz, $^3J_{H,H_b}$ = 10.3 Hz, $^2J_{H,P}$ = 7.3 Hz); 6.67—6.71 (m, 2 H, $C(3,5)_6H_4$); 7.17—7.26 (m, 4 H, $C(2,6)_6H_4$ + *m*-C_6H_5P); 7.29—7.35 (m, 1 H, *p*-C_6H_5P); 7.40—7.47 (m, 2 H, *o*-C_6H_5P); 7.47—7.57 (m, 3 H, *m*- + *p*-C_6H_5P); 7.86—7.93 (m, 2 H, *o*-C_6H_5P). $^1H\{^{31}P\}$ NMR ($CDCl_3$), δ: 1.93 (s, CH_3, 3 H); 2.88 (dd, 1 H, $C\underline{H}_aH_b$, $^3J_{H_a,H}$ = 2.6 Hz, $^2J_{H_a,H_b}$ = = 17.8 Hz); 3.26 (dd, 1 H, $CH_a\underline{H}_b$, $^3J_{H_b,H}$ = 10.3 Hz, $^2J_{H_b,H_a}$ = = 17.8 Hz); 3.70 (s, 3 H, CH_3O); 4.15 (dd, CHP, 1 H, $^3J_{H,H_a}$ = = 2.8 Hz, $^3J_{H,H_b}$ = 10.3 Hz); 6.66—6.72 (m, 2 H, $C(3,5)_6H_4$);

7.16—7.27 (m, 4 H, C(2,6)$_6$H$_4$ + *m*-C$_6$H$_5$P); 7.44 (d, 1 H, *p*-C$_6$H$_5$P, $^3J_{H,H}$ = 7.2 Hz); 7.47—7.57 (m, 3 H, *m*- + *p*-C$_6$H$_5$P); 7.90 (dd, 2 H, *o*-C$_6$H$_5$P, $^3J_{H,H}$ = 7.7 Hz, $^4J_{H,H}$ = 1.4 Hz). ^{13}C{^{1}H} NMR (150 MHz, CDCl$_3$), δ: 30.72 (s, C̲H$_3$C(O)), 40.19 (d, CH, $^1J_{C,P}$ = 69.7 Hz); 43.68 (s, CH$_2$); 55.14 (d, CH$_3$O, $^7J_{C,P}$ = 1.7 Hz); 113.81 (d, C(3,5)$_6$H$_4$, $^4J_{C,P}$ = 1.7 Hz); 127.63 (d, C(1)$_6$H$_4$, $^2J_{C,P}$ = 5.5 Hz); 128.12 (d, *m*-C$_6$H$_5$P, $^3J_{C,P}$ = 11.6 Hz); 128.87 (d, *m*-C$_6$H$_5$P, $^3J_{C,P}$ = 11.6 Hz); 130.74 (d, C(2,6)$_6$H$_4$, $^3J_{C,P}$ = 5.5 Hz); 131.00 (d, *o*-C$_6$H$_5$P, $^2J_{C,P}$ = 8.8 Hz); 131.29 (d, *o*-C$_6$H$_5$P, $^2J_{C,P}$ = 8.8 Hz); 131.42 (d, *p*-C$_6$H$_5$P, $^4J_{C,P}$ = 2.8 Hz); 131.57 (d, *ipso*-C$_6$H$_5$P, $^1J_{C,P}$ = 93.4 Hz); 131.62 (d, *ipso*-C$_6$H$_5$P, $^1J_{C,P}$ = 100.1 Hz); 131.97 (d, *p*-C$_6$H$_5$P, $^4J_{C,P}$ = 2.8 Hz); 158.61 (d, C(4)$_6$H$_4$, $^5J_{C,P}$ = 2.2 Hz); 205.58 (d, C=O, $^3J_{C,P}$ = 12.7 Hz).

4-(Diphenylphosphoryl)-4-(*p*-chlorophenyl)butan-2-one (7b). To a solution of 4-(*p*-chlorophenyl)but-3-en-2-one (**6b**) (2.07 g, 11.46 mmol) in benzene (10 mL), a solution of DPCP (2.46 g, 11.15 mmol) in benzene (5 mL) and a solution of glacial acetic acid (0.73 g, 12.16 mmol) in benzene (5 mL) were added dropwise in succession. The reaction mixture was kept for 48 h at ~20 °C, the solvent and other volatile substances were removed *in vacuo*, and the residue was dissolved in the minimum amount of ethanol and filtered through basic Al_2O_3 (5 g). Al_2O_3 was washed with ethanol (2×10 mL), the combined filtrates were evaporated until beginning of crystallization, and the precipitate that formed was separated and dried *in vacuo* (~10 Torr) for 1 h at 140 °C. The yield was 3.4 g (80.0%), m.p. 217—218 °C. Found (%): C, 68.79; H, 5.11; Cl, 9.15; P, 8.12. $C_{22}H_{20}ClO_2P$. Calculated (%): C, 69.02; H, 5.27; Cl, 9.26; P, 8.09. IR (KBr), ν/cm^{-1}: 1185, 1175 (P=O); 1715 (C=O). ^{31}P{^{1}H} NMR (400 MHz, CDCl$_3$), δ: 33.20 (s). ^{1}H NMR (CDCl$_3$), δ: 1.94 (s, 3 H, CH$_3$); 2.90 (ddd, 1 H, CH̲$_a$H$_b$, $^3J_{H_a,H}$ = 2.2 Hz, $^3J_{H_a,P}$ = 11.0 Hz, $^2J_{H_a,H_b}$ = 17.9 Hz); 3.25 (ddd, 1 H, CH$_a$H̲$_b$, $^3J_{H_b,H}$ = 10.2 Hz, $^3J_{H_b,P}$ = 5.1 Hz, $^2J_{H_b,H_a}$ = 18.0 Hz); 4.11—4.25 (m, 1 H, CHP); 7.12 (d, 2 H, C(3,5)$_6$H$_4$, $^3J_{H,H}$ = 8.1 Hz); 7.18—7.30 (m, 4 H, C(2,6)$_6$H$_4$ + *m*-C$_6$H$_5$P); 7.34 (t, 1 H, *p*-C$_6$H$_5$P, $^3J_{H,H}$ = 7.1 Hz); 7.39—7.60 (m, 5 H, *o*- + *m*- + *p*-C$_6$H$_5$P); 7.84—7.95 (m, 2 H, *o*-C$_6$H$_5$P). ^{1}H{^{31}P} NMR (400 MHz, CDCl$_3$), δ: 1.94 (s, 3 H, CH$_3$); 2.90 (dd, 1 H, CH̲$_a$H$_b$, $^3J_{H_a,H}$ = 2.9 Hz, $^2J_{H_a,H_b}$ = 18.2 Hz); 3.25 (dd, 1 H, CH$_a$H̲$_b$, $^3J_{H_b,H}$ = 10.4 Hz, $^2J_{H_b,H_a}$ = 18.1 Hz); 4.18 (dd, 1 H, CHP, $^3J_{H,H_a}$ = 2.5 Hz, $^3J_{H,H_b}$ = 10.2 Hz); 7.12 (d, 2 H, C(3,5)$_6$H$_4$, $^3J_{H,H}$ = 8.4 Hz); 7.19—7.29 (m, 4 H, C(2,6)$_6$H$_4$ + + *m*-C$_6$H$_5$P); 7.34 (t, 1 H, *p*-C$_6$H$_5$P, $^3J_{H,H}$ = 7.1 Hz); 7.45 (d, 2 H, *o*-C$_6$H$_5$P, $^3J_{H,H}$ = 7.3 Hz); 7.48—7.58 (m, 3 H, *m*- + + *p*-C$_6$H$_5$P); 7.90 (d, 2 H, *o*-C$_6$H$_5$P, $^3J_{H,H}$ = 7.1 Hz). ^{13}C{^{1}H} NMR (150 MHz, CDCl$_3$), δ: 30.59 (s, CH$_3$); 40.40 (d, CH, $^1J_{C,P}$ = 68.6 Hz); 43.57 (s, CH$_2$); 128.27 (d, *m*-C$_6$H$_5$P, $^3J_{C,P}$ = = 11.6 Hz); 128.53 (d, C(3,5)$_6$H$_4$, $^4J_{C,P}$ = 1.1 Hz); 128.99 (d, *m*-C$_6$H$_5$P, $^3J_{C,P}$ = 11.6 Hz); 130.86 (d, *o*-C$_6$H$_5$P, $^2J_{C,P}$ = = 8.8 Hz); 131.01 (d, C(2,6)$_6$H$_4$, $^3J_{C,P}$ = 6.1 Hz); 131.13 (d, *ipso*-C$_6$H$_5$P, $^1J_{C,P}$ = 96.0 Hz); 131.21 (d, *o*-C$_6$H$_5$P, $^2J_{C,P}$ = 8.3 Hz); 131.22 (d, *ipso*-C$_6$H$_5$P, $^1J_{C,P}$ = 99.0 Hz); 131.66 (d, *p*-C$_6$H$_5$P, $^4J_{C,P}$ = 2.8 Hz); 132.17 (d, *p*-C$_6$H$_5$P, $^4J_{C,P}$ = 2.8 Hz); 133.06 (d, C(4)$_6$H$_4$, $^5J_{C,P}$ = 2.8 Hz); 134.55 (d, C(1)$_6$H$_4$, $^2J_{C,P}$ = 5.5 Hz); 205.09 (d, C=O, $^3J_{C,P}$ = 13.3 Hz).

4-(Diphenylphosphoryl)-4-(thien-2-yl)butan-2-one (7c). To a solution of 4-(thien-2-yl)but-3-en-2-one (**6c**) (2.64 g, 0.0173 mol) in benzene (10 mL), a solution of DPCP (3.7 g, 0.0168 mol) in benzene (10 mL) and a solution of glacial acetic acid (1.1 g, 0.0183 mol) in benzene (20 mL) were added dropwise in succession. The reaction mixture was kept for 48 h at ~20 °C, the solvent and other volatile substances were removed *in vacuo*, the residue was dissolved in the minimum amount of boiling acetonitrile and cooled to 0 °C, the precipitate that formed was separated and recrystallized once more from acetonitrile. The yield was 3.5 g (58.8%), m.p. 165.0—165.5 °C. Found (%): C, 67.78; H, 5.41; P, 8.75; S, 9.04. $C_{20}H_{19}O_2PS$. Calculated (%): C, 67.78; H, 5.40; P, 8.74; S, 9.05. IR (KBr), ν/cm^{-1}: 1197, 1185 (P=O); 1709 (C=O). ^{31}P{^{1}H} NMR (CDCl$_3$), δ: 32.65 (s). ^{1}H NMR (400 MHz, CDCl$_3$), δ: 1.98 (s, 3 H, CH$_3$); 2.91 (ddd, 1 H, CH̲$_a$H$_b$, $^3J_{H_a,H}$ = 2.5 Hz, $^3J_{H_a,P}$ = 10.2 Hz, $^2J_{H_a,H_b}$ = 17.9 Hz); 3.25 (ddd, 1 H, CH$_a$H̲$_b$, $^3J_{H_b,H}$ = 10.3 Hz, $^3J_{H_b,P}$ = 5.0 Hz, $^2J_{H_b,H_a}$ = 17.7 Hz); 4.52—4.60 (m, 1 H, CHP); 6.79 (dd, 1 H, H(4)$_{thiophen}$, $^3J_{H,H}$ = 4.2 Hz, $^3J_{H,H}$ = 4.4 Hz); 6.87—6.93 (m, 1 H, H(3)$_{thiophen}$); 7.04 (d, 1 H, H(5)$_{thiophen}$, $^3J_{H,H}$ = 5.0 Hz); 7.29 (dt, 2 H, *m*-C$_6$H$_5$, $^3J_{H,H}$ = 7.4 Hz, $^4J_{H,P}$ = 2.6 Hz); 7.38 (t, 1 H, *p*-C$_6$H$_5$, $^3J_{H,H}$ = 7.2 Hz); 7.46—7.58 (m, 5 H, *o*- + *m*- + + *p*-C$_6$H$_5$); 7.84—7.93 (m, 2 H, *o*-C$_6$H$_5$). ^{1}H{^{31}P} NMR (400 MHz, CDCl$_3$), δ: 1.98 (s, 3 H, CH$_3$); 2.91 (dd, 1 H, CH̲$_a$H$_b$, $^3J_{H_a,H}$ = 2.1 Hz, $^2J_{H_a,H_a}$ = 17.7 Hz); 3.25 (dd, 1 H, CH$_a$H̲$_b$, $^3J_{H_b,H}$ = 10.3 Hz, $^2J_{H_b,H_a}$ = 17.7 Hz); 4.56 (dd, 1 H, CHP, $^3J_{H,H_a}$ = = 2.6 Hz, $^3J_{H,H_b}$ = 10.3 Hz); 6.79 (dd, 1 H, H(4)$_{thiophen}$, $^3J_{H,H}$ = = 3.8 Hz, $^3J_{H,H}$ = 4.8 Hz); 6.90 (d, 1 H, H(3)$_{thiophen}$, $^3J_{H,H}$ = = 2.9 Hz); 7.04 (d, 1 H, H(5)$_{thiophen}$, $^3J_{H,H}$ = 4.9 Hz); 7.29 (t, 2 H, *m*-C$_6$H$_5$, $^3J_{H,H}$ = 7.5 Hz); 7.38 (t, 1 H, *p*-C$_6$H$_5$, $^3J_{H,H}$ = = 7.3 Hz); 7.46—7.58 (m, 5 H, *o*- + *m*- + *p*-C$_6$H$_5$); 7.88 (d, 2 H, *o*-C$_6$H$_5$, $^3J_{H,H}$ = 6.9 Hz). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$), δ: 30.47 (s, CH$_3$); 36.44 (d, CH, $^1J_{C,P}$ = 70.4 Hz); 44.21 (s, CH$_2$); 124.78 (d, CH$_{thiophen}$, $J_{C,P}$ = 2.9 Hz); 126.62 (d, CH$_{thiophen}$, $J_{C,P}$ = 2.6 Hz); 127.18 (d, CH$_{thiophen}$, $J_{C,P}$ = 6.6 Hz); 128.06 (d, *m*-C$_6$H$_5$, $^3J_{C,P}$ = 11.7 Hz); 128.79 (d, *m*-C$_6$H$_5$, $^3J_{C,P}$ = 11.4 Hz); 130.79 (d, *ipso*-C$_6$H$_5$, $^1J_{C,P}$ = 101.2 Hz); 130.85 (d, *ipso*-C$_6$H$_5$, $^1J_{C,P}$ = 95.0 Hz); 130.95 (d, *o*-C$_6$H$_5$, $^2J_{C,P}$ = 8.8 Hz); 131.16 (d, *o*-C$_6$H$_5$, $^2J_{C,P}$ = 8.8 Hz); 131.56 (d, *p*-C$_6$H$_5$, $^4J_{C,P}$ = 2.9 Hz); 132.02 (d, *p*-C$_6$H$_5$, $^4J_{C,P}$ = 2.9 Hz); 137.34 (d, C(2)$_{thiophen}$, $^2J_{C,P}$ = 6.2 Hz); 204.86 (d, C=O, $^3J_{C,P}$ = 12.1 Hz).

4-(Diphenylphosphoryl)-4-(fur-2-yl)butan-2-one (7d). To a solution of 4-(fur-2-yl)but-3-en-2-one (**6d**) (2.4 g, 0.0176 mol) in benzene (10 mL), a solution of DPCP (3.7 g, 0.0168 mol) in benzene (10 mL) and a solution of glacial acetic acid (1.1 g, 0.0183 mol) in benzene (20 mL) were added dropwise in succession. The reaction mixture was kept for 48 h at ~20 °C, the solvent and other volatile substances were removed *in vacuo*, and the residue was dissolved in ethyl acetate (20 mL) and filtered through basic Al_2O_3 (6 g). Al_2O_3 was washed with ethyl acetate (2×10 mL), the combined filtrates were concentrated until the volume of 10 mL and kept for 12 h at ~20 °C, and the precipitate that formed was separated, recrystallized from ethyl acetate, and dried *in vacuo* (~1 Torr) for 1 h at 100 °C. The yield was 4.2 g (74.0%), m.p. 125.0—125.5 °C. Found (%): C, 71.07; H, 5.67; P, 9.08. $C_{20}H_{19}O_3P$. Calculated (%): C, 71.00; H, 5.66; P, 9.15. IR (KBr), ν/cm^{-1}: 1203, 1190 (P=O); 1714 (C=O). ^{31}P{^{1}H} NMR (CDCl$_3$), δ: 32.13 (s). ^{1}H NMR (400 MHz, CDCl$_3$), δ: 2.04 (s, 3 H, CH$_3$); 2.97 (ddd, 1 H, CH̲$_a$H$_b$, $^3J_{H_a,H}$ = = 3.1 Hz, $^3J_{H_a,P}$ = 10.0 Hz, $^2J_{H_a,H_b}$ = 18.0 Hz); 3.23 (ddd, 1 H, CH$_a$H̲$_b$, $^3J_{H_b,H}$ = 10.6 Hz, $^3J_{H_b,P}$ = 5.5 Hz, $^2J_{H_b,H_a}$ = 18.0 Hz); 4.47 (ddd, 1 H, CHP, $^3J_{H,H_a}$ = 3.0 Hz, $^3J_{H,H_b}$ = 10.7 Hz, $^2J_{H,P}$ = = 10.7 Hz); 5.97 (dd, 1 H, H(3)$_{furan}$, $^3J_{H,H}$ = 3.1 Hz, $^4J_{H,P}$ = 3.1 Hz); 6.16 (dd, 1 H, H(4)$_{furan}$, $^3J_{H,H}$ = 2.8 Hz, $^3J_{H,H}$ = 2.1 Hz); 7.16 (br.s, 1 H, H(5)$_{furan}$); 7.34 (dt, 2 H, *m*-C$_6$H$_5$, $^3J_{H,H}$ = 7.6 Hz, $^4J_{H,P}$ = 3.0 Hz); 7.40—7.58 (m, 6 H, *o*- + *m*- + *p*-C$_6$H$_5$); 7.77—7.86 (m, 2 H, *o*-C$_6$H$_5$). ^{1}H{^{31}P} NMR (400 MHz CDCl$_3$), δ: 2.04 (s, 3 H, CH$_3$); 2.97 (dd, 1 H, CH̲$_a$H$_b$, $^3J_{H_a,H}$ = 3.0 Hz,

$^2J_{H_a,H_b}$ = 18.0 Hz); 3.23 (dd, 1 H, $CH_a\underline{H}_b$, $^3J_{H_a,H}$ = 10.5 Hz, $^2J_{H_a,H_a}$ = 18.0 Hz); 4.47 (dd, 1 H, CHP, $^3J_{H,H_a}$ = 3.1 Hz, $^3J_{H,H_b}$ = 10.5 Hz); 5.97 (d, 1 H, $H(3)_{furan}$, $^3J_{H,H}$ = 3.2 Hz); 6.16 (dd, 1 H, $H(4)_{furan}$, $^3J_{H,H}$ = 3.0 Hz, $^3J_{H,H}$ = 2.0 Hz); 7.16 (d, 1 H, $H(5)_{furan}$, $^3J_{H,H}$ = 1.6 Hz); 7.34 (t, 2 H, *m*-C_6H_5, $^3J_{H,H}$ = 7.6 Hz); 7.44 (t, 1 H, *p*-C_6H_5, $^3J_{H,H}$ = 7.5 Hz); 7.47—7.57 (m, 5 H, *o*- + + *m*- + *p*-C_6H_5); 7.78—7.85 (m, 2 H, *o*-C_6H_5). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$), δ: 30.05 (s, CH_3); 35.72 (d, CH, $^1J_{C,P}$ = = 70.4 Hz); 40.67 (s, CH_2); 108.57 (d, $C(3)H_{furan}$, $^3J_{C,P}$ = 6.2 Hz); 110.62 (d, $C(4)H_{furan}$, $^4J_{C,P}$ = 2.9 Hz); 128.09 (d, *m*-C_6H_5, $^3J_{C,P}$ = 11.7 Hz); 128.65 (d, *m*-C_6H_5, $^3J_{C,P}$ = 11.7 Hz); 130.35 (d, *ipso*-C_6H_5, $^1J_{C,P}$ = 100.5 Hz); 130.97 (d, *ipso*-C_6H_5, $^1J_{C,P}$ = = 96.8 Hz); 131.20 (d, *o*-C_6H_5, $^2J_{C,P}$ = 9.2 Hz); 131.73 (d, *p*-C_6H_5, $^4J_{C,P}$ = 2.9 Hz); 132.02 (d, *p*-C_6H_5, $^4J_{C,P}$ = 2.6 Hz); 141.64 (d, $C(5)H_{furan}$, $^4J_{C,P}$ = 2.9 Hz); 148.73 (d, $C(2)_{furan}$, $^2J_{C,P}$ = 6.6 Hz); 204.83 (d, C=O, $^3J_{C,P}$ = 12.1 Hz).

(*E*)-4-(Diphenylphosphoryl)but-3-en-2-one (9). To a solution of 90% 4-methoxybut-3-en-2-one (**8**) (1.87 g, 0.0168 mol) in benzene (10 mL), a solution of DPCP (3.7 g, 0.0168 mol) in benzene (10 mL) and a solution of glacial acetic acid (1.1 g, 0.0183 mol) in benzene (20 mL) were added dropwise in succession. The reaction mixture was kept for 48 h at ~20 °C, the solvent and other volatile substances were removed *in vacuo*, the residue was washed with hot heptane and dissolved in benzene (20 mL), the resulted solution was filtered through silica gel (6 g), the silica gel was washed with benzene (2×10 mL), the combined filtrates were concentrated until the volume of ~15 mL and kept for 12 h at ~20 °C, and the precipitate that formed was separated, recrystallized from benzene, and dried *in vacuo* (~10 Torr) for 3 h at 100 °C. The yield was 2.6 g (57.3%), m.p. 131.5—132.5 °C (*cf.* Ref. 23: m.p. 128—129 °C). Found (%): C, 71.21; H, 5.63; P, 11.67. $C_{16}H_{15}O_2P$. Calculated (%): C, 71.11; H, 5.59; P, 11.46. IR (KBr), ν/cm^{-1}: 1185 (P=O); 1693, 1701 pl. (C=O); 1604 (C=C). $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ: 22.71 (s). ^1H NMR (400 MHz, $CDCl_3$), δ: 2.35 (s, 3 H, CH_3); 7.03 (dd, 1 H, PCH=C$\underline{H}$, $^3J_{H,H}$ = 17.3 Hz, $^3J_{H,P}$ = 17.8 Hz); 7.31 (dd, 1 H, PC$\underline{H}$=CH, $^3J_{H,H}$ = 17.1 Hz, $^2J_{H,P}$ = 22.2 Hz); 7.44—7.51 (m, 4 H, *m*-C_6H_5); 7.52—7.58 (m, 2 H, *p*-C_6H_5); 7.64—7.72 (m, 4 H, *o*-C_6H_5). $^1H\{^{31}P\}$ NMR (400 MHz, $CDCl_3$), δ: 2.34 (s, 3 H, CH_3); 7.03 (d, 1 H, PCH=C$\underline{H}$, $^3J_{H,H}$ = 17.1 Hz); 7.31 (d, 1 H, PC$\underline{H}$=CH, $^3J_{H,H}$ = 17.0 Hz); 7.47 (t, 4 H, *m*-C_6H_5, $^3J_{H,H}$ = = 7.4 Hz); 7.55 (t, 2 H, *p*-C_6H_5, $^3J_{H,H}$ = 7.4 Hz); 7.68 (d, 4 H, *o*-C_6H_5, $^3J_{H,H}$ = 7.7 Hz). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$), δ: 28.79 (s, CH_3); 128.75 (d, *m*-C_6H_5, $^3J_{C,P}$ = 12.5 Hz); 131.02 (d, *ipso*-C_6H_5, $^1J_{C,P}$ = 107.1 Hz); 131.17 (d, *o*-C_6H_5, $^2J_{C,P}$ = = 10.3 Hz); 132.33 (d, *p*-C_6H_5, $^4J_{C,P}$ = 2.9 Hz); 135.14 (d, P$\underline{C}$H=CH, $^1J_{C,P}$ = 93.2 Hz); 142.62 (d, PCH=$\underline{C}$H, $^2J_{C,P}$ = = 2.2 Hz); 196.18 (d, C=O, $^3J_{C,P}$ = 17.2 Hz).

(*E*)-5-(Diphenylphosphoryl)-1,5-diphenylpent-1-en-3-one (11). To a solution of *trans*,*trans*-dibenzylideneacetone (**10**) (2.61 g, 11.14 mmol) in benzene (20 mL), a solution of DPCP (2.46 g, 11.14 mmol) in benzene (5 mL) and a solution of glacial acetic acid (0.73 g, 12.16 mmol) in benzene (5 mL) were added dropwise in succession. The reaction mixture was kept for 48 h at ~20 °C, the precipitate that formed was separated, recrystallized from acetonitrile, and dried *in vacuo* (10 Torr) for 3 h at 140 °C. The yield was 4.0 g (82.3%), m.p. 221—222 °C. Found (%): C, 79.85; H, 5.82; P, 7.11. $C_{29}H_{25}O_2P$. Calculated (%): C, 79.80; H, 5.77; P, 7.10. IR (KBr), ν/cm^{-1}: 1186, 1174 (P=O); 1690, 1649 (C=O); 1625, 1615 (C=C). $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ: 34.19 (s). ^1H NMR ($CDCl_3$), δ: 3.12 (ddd, 1 H, $C\underline{H}_aH_b$, $^3J_{H_a,H}$ = 2.6 Hz, $^3J_{H_a,P}$ = 11.0 Hz, $^2J_{H_a,H_b}$ = 17.5 Hz); 3.68 (ddd, 1 H, $CH_a\underline{H}_b$, $^3J_{H_b,H}$ = 10.4 Hz, $^3J_{H_b,P}$ = 5.0 Hz, $^2J_{H_b,H_a}$ = = 17.6 Hz); 4.36 (ddd, 1 H, CHP, $^3J_{H,H_a}$ = 2.6 Hz, $^3J_{H,H_b}$ = 10.1 Hz, $^2J_{H,P}$ = 7.1 Hz); 6.52 (d, 1 H, C(O)C$\underline{H}$=CH, $^3J_{H,H}$ = 16.4 Hz); 7.06—7.56 (m, 19 H, C_6H_5 + C(O)CH=C$\underline{H}$); 7.93—8.02 (m, 2 H, *o*-C_6H_5P). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$), δ: 40.40 (s, CH_2); 41.14 (d, CH, $^1J_{C,P}$ = 69.1 Hz); 126.05 (s, C(O)$\underline{C}$H=CH); 127.12 (d, *p*-C_6H_5CP, $^5J_{C,P}$ = 2.2 Hz); 128.10 (d, *m*-C_6H_5P, $^3J_{C,P}$ = = 11.6 Hz); 128.33 (s, *m*-C_6H_5CH=CH); 128.34 (d, *m*-C_6H_5CP, $^4J_{C,P}$ = 3.3 Hz); 128.96 (s, *o*-C_6H_5CH=CH); 128.98 (d, *m*-C_6H_5P, $^3J_{C,P}$ = 11.0 Hz); 129.82 (d, *o*-C_6H_5CP, $^3J_{C,P}$ = 6.1 Hz); 130.71 (s, *p*-C_6H_5CH=CH); 130.96 (d, *o*-C_6H_5P, $^2J_{C,P}$ = 8.8 Hz); 131.33 (d, *o*-C_6H_5P, $^2J_{C,P}$ = 8.0 Hz); 131.40 (d, *ipso*-C_6H_5P, $^1J_{C,P}$ = 94.5 Hz); 131.45 (d, *p*-C_6H_5P, $^4J_{C,P}$ = 2.8 Hz); 131.60 (d, *ipso*-C_6H_5P, $^1J_{C,P}$ = 100.6 Hz); 132.08 (d, *p*-C_6H_5P, $^4J_{C,P}$ = = 2.8 Hz); 134.14 (s, *ipso*-C_6H_5CH=CH); 135.83 (d, *ipso*-C_6H_5CP, $^2J_{C,P}$ = 6.1 Hz); 143.57 (s, $C_6H_5\underline{C}$H=CH); 196.76 (d, C=O, $^3J_{C,P}$ = 13.3 Hz).

3-[α-(Diphenylphosphoryl)benzyl]pentan-2,4-dione (13). To a solution of 3-benzylidenepentan-2,4-dione (**12**) (2.16 g, 11.15 mmol) in benzene (10 mL), a solution of DPCP (2.46 g, 11.14 mmol) in benzene (5 mL) and a solution of glacial acetic acid (0.73 g, 12.16 mmol) in benzene (5 mL) were added dropwise in succession. The reaction mixture was kept for 48 h at ~20 °C and the precipitate that formed was separated, recrystallized from ethyl acetate, and dried *in vacuo* (10 Torr) for 2 h at 120 °C. The yield was 3.7 g (85.1%), m.p. 189—190 °C (cf. Ref. 24: m.p. 182—184 °C). Found (%): C, 73.88; H, 5.69; P, 7.95. $C_{24}H_{23}O_3P$. Calculated (%): C, 73.83; H, 5.94; P, 7.93. IR (KBr), ν/cm^{-1}: 1177, 1165 pl. (P=O); 1724, 1703 (C=O). IR ($CDCl_3$), ν/cm^{-1}: 1184 (P=O); 1736, 1724, 1700 (C=O). $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ: 31.56 (s). ^1H NMR (600 MHz, $CDCl_3$), δ: 1.81 (s, 3 H, CH_3); 2.12 (s, 3 H, CH_3); 4.81 (dd, 1 H, CHP, $^3J_{H,H}$ = 11.2 Hz, $^2J_{H,P}$ = 9.6 Hz); 4.86 (dd, 1 H, C$\underline{H}$CHP, $^3J_{H,H}$ = 11.1 Hz, $^3J_{H,P}$ = 10.5 Hz); 6.98—7.05 (m, 2 H, C_6H_5C); 7.07—7.14 (m, 3 H, C_6H_5C); 7.26 (dt, 2 H, *m*-C_6H_5P, $^3J_{H,H}$ = = 7.7 Hz, $^4J_{H,P}$ = 3.1 Hz); 7.38 (dt, 1 H, *p*-C_6H_5P, $^3J_{H,H}$ = 7.5 Hz, $^5J_{H,P}$ = 1.3 Hz); 7.40—7.45 (m, 2 H, *o*-C_6H_5P); 7.48—7.53 (m, 2 H, *m*-C_6H_5P); 7.56 (dt, 1 H, *p*-C_6H_5P, $^3J_{H,H}$ = 7.4 Hz, $^5J_{H,P}$ = 1.4 Hz); 7.86—7.93 (m, 2 H, *o*-C_6H_5P). $^1H\{^{31}P\}$ NMR ($CDCl_3$), δ: 1.78 (s, 3 H, CH_3); 2.09 (s, 3 H, CH_3); 4.78 (d, 1 H, CHP, $^3J_{H,H}$ = 11.3 Hz); 4.83 (d, 1 H, C$\underline{H}$CHP, $^3J_{H,H}$ = 11.2 Hz); 6.95—7.02 (m, 2 H, C_6H_5C); 7.03—7.11 (m, 3 H, C_6H_5C); 7.23 (t, 2 H, *m*-C_6H_5P, $^3J_{H,H}$ = 7.6 Hz); 7.31—7.42 (m, 3 H, *o*- + + *p*-C_6H_5P); 7.44—7.57 (m, 3 H, *m*- + *p*-C_6H_5P); 7.83—7.90 (m, 2 H, *o*-C_6H_5P). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$), δ: 28.30 (s, CH_3); 30.61 (s, CH_3); 47.05 (d, CHP, $^1J_{C,P}$ = 63.6 Hz); 68.77 (s, $\underline{C}$HCHP); 127.53 (d, *p*-C_6H_5C, $^5J_{C,P}$ = 2.9 Hz); 127.97 (d, *m*-C_6H_5P, $^3J_{C,P}$ = 11.6 Hz); 128.52 (d, *m*-C_6H_5C, $^4J_{C,P}$ = = 2.2 Hz); 128.58 (d, *m*-C_6H_5P, $^3J_{C,P}$ = 11.6 Hz); 129.82 (d, *ipso*-C_6H_5P, $^1J_{C,P}$ = 100.1 Hz); 130.23 (d, *o*-C_6H_5C, $^3J_{C,P}$ = 4.4 Hz); 131.44 (d, *ipso*-C_6H_5P, $^1J_{C,P}$ = 95.1 Hz); 131.69 (d, *p*-C_6H_5P, $^4J_{C,P}$ = 2.8 Hz); 131.72 (d, *o*-C_6H_5P, $^2J_{C,P}$ = 8.3 Hz); 131.93 (d, *o*-C_6H_5P, $^2J_{C,P}$ = 8.8 Hz); 132.23 (d, *p*-C_6H_5P, $^4J_{C,P}$ = 2.8 Hz); 133.72 (d, *ipso*-C_6H_5C, $^2J_{C,P}$ = 5.0 Hz); 201.56 (s, C=O); 201.60 (d, C=O, $^3J_{C,P}$ = 12.2 Hz).

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References

1. V. F. Mironov, D. A. Tatarinov, T. A. Baronova, A. I. Konovalov, A. A. Kostin, V. I. Kryshtob, RF. Pat. 2374260, *Byull. Izobret.*, 2009, 11.
2. A. M. Safiullina, A. G. Matveeva, T. K. Dvoryanchikova, O. A. Sinegribova, A. M. Tu, A. A. Kostin, V. F. Mironov, I. G. Tananaev, *Russ. Chem. Bull.* (*Int. Ed.*), 2012, **61**, 392 [*Izv. Akad. Nauk, Ser. Khim.*, 2012, 390].
3. P. S. Lemport, G. V. Bodrin, M. P. Pasechnik, A. G. Matveeva, P. V. Petrovskii, A. V. Vologzhanina, E. E. Nifant´ev, *Russ. Chem. Bull.* (*Int. Ed.*), 2007, **56**, 1911 [*Izv. Akad. Nauk, Ser. Khim.*, 2007, 1846].
4. P. S. Lemport, G. V. Bodrin, A. I. Belyakov, P. V. Petrovskii, A. V. Vologzhanina, E. E. Nifant´ev, *Mendeleev Commun.*, 2009, **19**, 303.
5. C. A. Kingsbury, D. Thoennes, *Tetrahedron Lett.*, 1976, **17**, 3037.
6. C. A. Kingsbury, D. J. Cram, *J. Am. Chem. Soc.*, 1960, **82**, 1810.
7. K. B. Sharpless, R. F. Lauer, A. Y. Teranishi, *J. Am. Chem. Soc.*, 1973, **95**, 6137.
8. R. W. King, C. H. Depuy, *Chem. Rev.*, 1960, **60**, 431.
9. J. B. Conant, J. B. S. Braverman, R. E. Hussey, *J. Am. Chem. Soc.*, 1923, **45**, 165.
10. A. Bell, A. H. Davidson, C. Earnshaw, H. K. Norrish, R. S. Torr, D. B. Trowbridge, S. Warren, *J. Chem. Soc.*, *Perkin Trans. 1*, 1983, 2879.
11. M. Mikoiajczyk, A. Zatorski, *J. Org. Chem.*, 1991, **56**, 1217.
12. I. V. Bakhtiyarova, V. I. Galkin, R. A. Cherkasov, Kh. Kurdi, A. N. Pudovik, *Dokl. Chem.* (*Engl. Transl.*), 1989, **308** [*Dokl. Akad. Nauk SSSR*, 1989, **308**, 1135].
13. A. N. Pudovik, A. A. Sobanov, I. V. Bakhtiyarova, M. G. Zimin, *J. Gen. Chem. USSR* (*Engl. Transl.*), 1983, **53** [*Zh. Obshsch. Khim.*, 1983, **53**, 2456].
14. D. Semenzin, G. Etemad-Moghadam, D. Albouy, O. Diallo, M. Koenig, *J. Org. Chem.*, 1997, **62**, 2414.
15. J. A. Miller, D. Stewart, *Tetrahedron Lett.*, 1977, **18**, 1065.
16. K. R. Hanson, *J. Am. Chem. Soc.*, 1966, **88**, 2731.
17. K. Mislow, M. Raban, *Top. Stereochem.*, 1967, **1**, 1.
18. L. J. Bellamy, *Infrared Spectra of Complex molecules*, London, John Wiley, 1954, 204.
19. M. L. Martin, R. Mantione, G. J. Martin, *Tetrahedron Lett.*, 1966, 3873.
20. M. Brink, *Tetrahedron Lett.*, 1969, **10**, 4055.
21. M. Brink, *Tetrahedron*, 1971, **27**, 143.
22. E. I. Goryunov, P. V. Petrovskii, I. Yu. Kudryavtsev, L. S. Zakharov, M. I. Kabachnik, *Dokl. Akad. Nauk SSSR*, 1985, **281**, 1378 [*Dokl. Chem.* (*Engl. Transl.*), 1985, **281**].
23. S. D. Darling, S. J. Brandes, *J. Org. Chem.*, 1982, **47**, 1413.
24. F. Ramirez, J. F. Pilot, O. P. Madan, C. P. Smith, *J. Am. Chem. Soc.*, 1968, **90**, 1275.
25. Aung Myo Tu, A. M. Safiullina, O. A. Sinegribova, G. V. Bodrin, E. I. Goryunov, I. B. Goryunova, A. G. Matveeva, E. E. Nifant´ev, *The IV International Young School Conference on Physical Chemistry of Crown Compounds*, *Porphyrins*, *and Phtalocyanins* (*Tuapse, September 17—21, 2012*), Book of Abstracts, 26.
26. D. N. Laikov, *Chem. Phys. Lett.*, 1997, **281**, 151.
27. D. N. Laikov, Yu. A. Ustynyuk, *Russ. Chem. Bull.* (*Int. Ed.*), 2005, **54**, 820 [*Izv. Akad. Nauk, Ser. Khim.*, 2005, 804].
28. J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.
29. K. Zumbansen, A. Döhring, B. List, *Adv. Synth. Catal.*, 2010, **352**, 1135.
30. A. Weisberger, E. Proskayer, J. Riddik, E. Toops, *Organic Solvents*, 1958.

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