Heteroatom Chemistry
Volume 8, Number 3, 1997

Functionalized Phospholanes and Phosphorinanes from 1,4- and 1,5-Diketones

Vladimir I. Vysotskii

Far Eastern State University, 2-9, Oktyabrskaya Street, Vladivostok, 690091, Russia

Received 10 April 1996; revised 17 July 1996

ABSTRACT

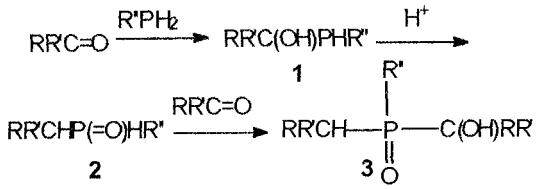
Phosphorylation reactions of 1,4-diketones, 1,5-diketones, and methylene-1,5-diketones with bidentate phosphorus nucleophiles (phosphines and phosphonous acid derivatives) represent convenient methods of synthesis of saturated functionalized phospholanes and phosphorinanes. © 1997 John Wiley & Sons, Inc. Heteroatom Chem **8***: 217–223, 1997.*

INTRODUCTION

We wish to present results of our explorations in the phosphorus organic heterocycles area from 1980 to 1995. The general theme of our investigations involves the chemistry of 1,4- and 1,5-diketones. These compounds are among the best starting materials available for synthesis of nitrogen, oxygen, and sulfur heterocycles. We explored the reactions of 1,4- and 1,5-diketones with compounds of the H_2X-type, where X = PH, PPh, POOH, etc.

REACTIONS OF 1,4- and 1,5-DIKETONES WITH PHOSPHINE, PHENYLPHOSPHINE, AND DIPHENYLPHOSPHINE

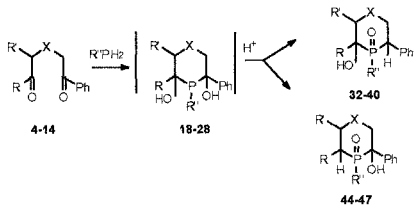
Ketones have been reported to react with phosphine and phenylphosphine in acidic media [1,2]. The first step of this reaction is the nucleophilic addition of the phosphine to the carbonyl group (intermediate **1**); the next stage is the hydroxyphosphine-phosphine oxide rearrangement (intermediate **2**) and then combination with a second molecule of ketone to give the alkyl-α-hydroxyalkyl-phosphine oxide as the final product **3**:



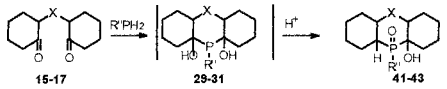
We expanded this reaction to 1,4-diketones **4–7,15** and 1,5-diketones **8–14,16**. Dihydroxyphospholanes **18–21,29** (R″ = H, Ph) and dihydroxy-phosphorinanes **22–28,30** (R″ = H, Ph) were formed as intermediates as we anticipated, and 2-hydroxy-1-oxophospholanes **32–35,41,44,45** (R″ = H, Ph) and 2-hydroxy-1-oxophosphorinanes **36–40,43,46,47** (R″ = H, Ph) were obtained, respectively, as final reaction products [3–7]. The earlier workers [1,2] claimed the order of steps of phosphorylation of ketones to be addition, rearrangement, addition. We proposed a different order: addition, addition, rearrangement. The diketone **12**, for example, must add the phosphine or the phenylphosphine to the more active *cyclic* carbonyl group.

Dedicated to Prof. Louis Quin on the occasion of his retirement from the University of Massachusetts.

© 1997 John Wiley & Sons, Inc.
1042-7163/97/030217-07

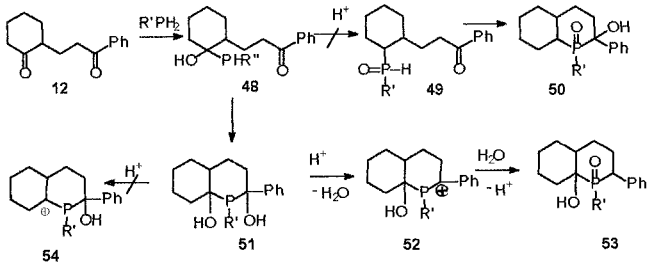


	R	R'	X
4, 18, 32	Ph	H	-
5, 19, 33, 44	Me	H	-
6, 20, 34	-(CH2)3-		-
7, 21, 35, 45	-(CH2)4-		-
8, 22, 36	Ph	H	CH2
9, 23, 37	Ph	H	CHPh
10, 24, 46	-(CH2)3-		CH2
11, 25, 47	-(CH2)3-		CHPh
12, 26, 38	-(CH2)4-		CH2
13, 27, 39	-(CH2)4-		CHPh
14, 28, 40	-CH2-CMe2-O-CH2		CHPh

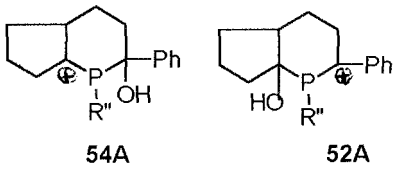


X = - (**15, 29, 41**), CHPh (**16, 30, 42**), S (**17, 31, 43**)

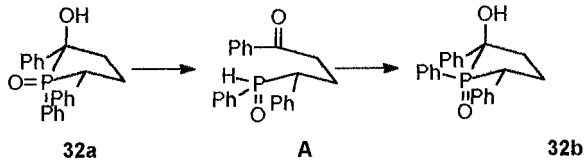
R" = H, Ph



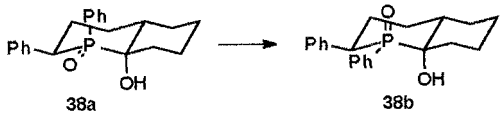
According to the earlier concept, adduct **48** would give compound **49**, and if the next step were rearrangement, the latter would cyclize to the phosphorinane **50**. However, this compound was not obtained. The actual experiments gave compounds **53** that were obtained with yields of 79% (if R″ = H) and 80% (if R″ = Ph). These compounds could be synthesized from intermediates **51**, the product of the second addition, and **52**, this benzylic ion being more stable than ion **54**. Thus, the addition, addition product **51** must be synthesized before rearrangement occurs. The compounds **46,47** (R″ = H, Ph) were obtained from semicyclic diketones **10,11**. The order addition, rearrangement, addition can be realized in these cases, but we assume that an addition, addition, rearrangement order is also suitable in these reactions. The intermediates of the **51** type can be formed in these cases, and they give ions **52A** or **54A** after dehydration in acidic media. Only **54A** led to **46,47**. We suppose that **54A** is more stable than **52A**, because staggered interactions disappear in the five-membered ring of this ion.



The reactions of 1,4- and 1,5-diketones with phosphine and phenylphosphine are not stereoselective and lead to stereoisomeric mixtures. The main stereoisomers have the highest melting points and maximum equatorial substituents. We observed a "double melting point" phenomenon when the low-melting isomer was transformed into the high-melting isomer by heating. Two examples are shown below. The stereoisomer **32a** melted at 148 °C then crystallized and melted at 210 °C [4]. There was conversion to stereoisomer **32b** at this point as chromatographic data demonstrated. We think that stereoisomer **32a** opens at the five-membered ring (intermediate **A**), the configuration of the P-center inverts, and the new intermediate cyclizes to **32b**:

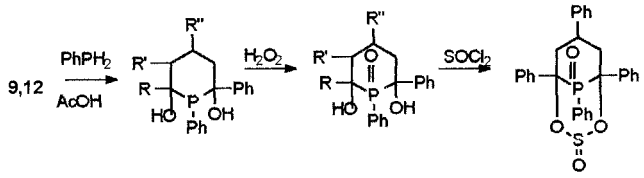


Similarly, stereoisomer **38a** melted at 237–239 °C, crystallized, and then melted at 288–289 °C, giving compound **38b** [6]:



We assume that an opening of the ring also occurred in this case.

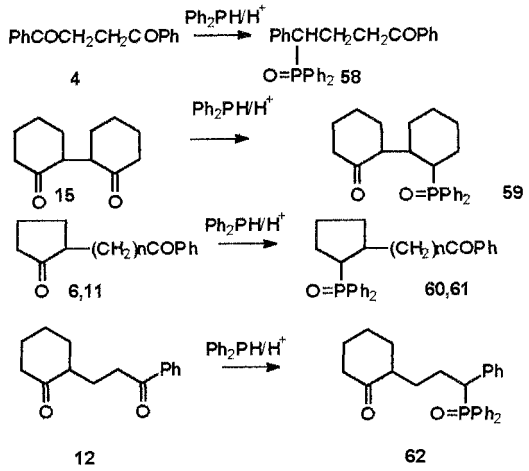
Diketones **9** or **12** and phenylphosphine form unstable compounds **23** or **26** if they react in acetic acid [6]. Compounds **23** and **26** were oxidized to the oxides **55** and **56** by action of oxygen of the air or by hydrogen peroxide; the former gave the cyclic sulfite **57** with thionyl chloride. We conclude that the hydroxyl groups in six-membered rings of **22–28** were *cis*-diaxial. Karaulov and co-workers [8] confirmed this conclusion, and they synthesized a cyclic sulfite from compound **31** (R = Ph).



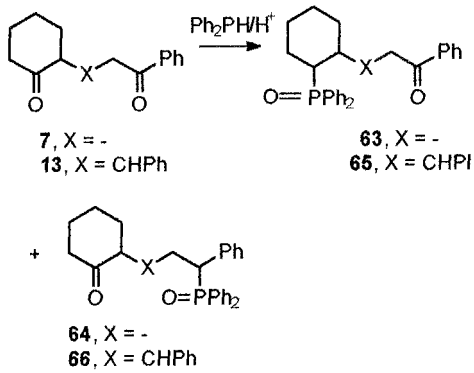
23,26 55,56 57

R = R" = Ph, R' = H (23,55); R+R' = $(CH_2)_4$, R" = H (26,56)

Diketones **4**, **6**, **7**, **11–13**, and **15** reacted with diphenylphosphine and gave the oxoalkyldiphenylphosphine oxides, even when an excess of diphenylphosphine was used [9,10]. The oxoalkyldiphenylphosphine oxides **58,59** were synthesized from symmetrical 1,4-diketones **4** and **15**, respectively. 1,4-Diketone **6** (n = 1) and 1,5-diketone **11** (n = 2) gave products **60,61** with diphenylphosphine oxide substituents in the five-membered rings.

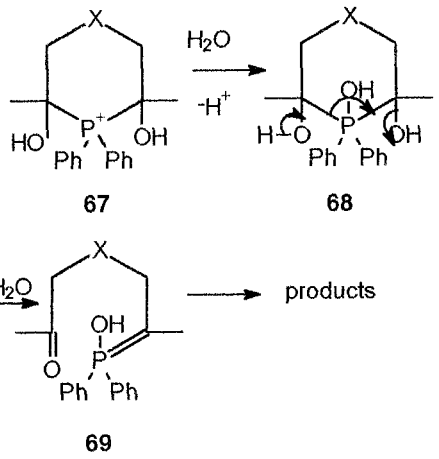


1,5-Diketone **12** reacted with diphenylphosphine to give product **62**.



7, X = -
13, X = CHPh
63, X = -
65, X = CHPh
64, X = -
66, X = CHPh

Diketones **7** and **13** were converted into mixtures of position isomers **63,64** (ratio = 6:1) and **65,66** (ratio = 1:3.5), respectively. We assume that cation **67** is an intermediate in this reaction.



67 **68**

69

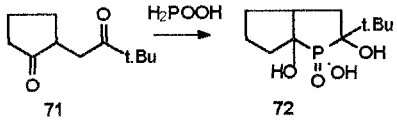
The hydroxyl group adds to the phosphorus atom, and the ion **67** is converted into hydroxy-phosphorane **68** that loses a molecule of water to give **69**. This isomerizes to the oxoalkyldiphenylphosphine oxide.

Reaction of 1,4- and 1,5-Diketones with Phosphonous Acid and Its Esters

As described in early work [11], phosphonous acid reacts with two molecules of acetone to form dihydroxyphosphinic acid **70**:

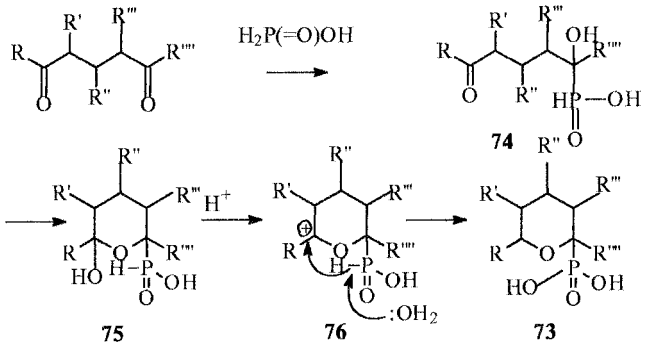
$$H_2POOH + 2CH_3COCH_3 \rightarrow \rightarrow (CH_3)_2C(OH)]_2POOH$$
70

The reaction of diketone **71** with phosphonous acid takes an analogous course, the 1,2,5-dihydroxyphospholane **72** being the main product [12]:



71 **72**

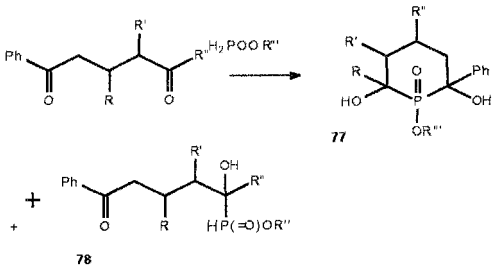
However, the reaction of 1,5-diketones with phosphonous acid, in acetic acid as solvent, has another result, the tetrahydropyranyl-2-phosphonic acids **73** being synthesized [13,14]:



75 **76** **73**

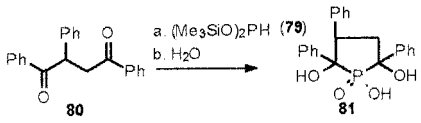
As we proposed, the first step of this reaction is the addition of phosphonous acid to the carbonyl group with formation of the compound **74**. The latter cyclizes to the hydroxytetrahydropyran **75**, which loses a molecule of water in the acidic media to form the cation **76**. A hydride shift takes place in the cation **76**, and the final product **73** is formed after addition of a molecule of water to **76**.

As we experienced failure in an attempt to synthesize hydroxyphosphorinanes by the reaction of 1,5-diketones with phosphonous acid, we examined the reaction of 1,5-diketones with alkyl hypophosphites [15].



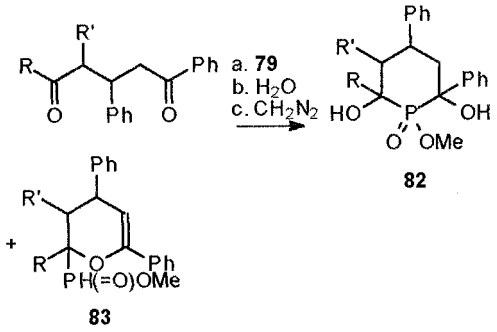
The products of this reaction were dihydroxyphosphorinanes **77** and α-hydroxy-ε-oxo-pentylphosphinic acids esters **78**. The latter were converted into compounds **73** by heating with acids.

Synthesis of compounds **77** with alkyl hypophosphites is not convenient because alkyl hypophosphites are unstable compounds. Therefore, we used the bis(trimethylsilyl) phosphonite **79** as a reagent in the synthesis of 2,5-dihydroxyphospholanes from 1,4-diketones and 2,6-dihydroxyphosphorinanes from 1,5-diketones. The reaction of 1,2,4-triphenyl-1,4-butanedione **80** with reagent **79** gave compound **81** (after hydrolysis; yield 99%) [16]:



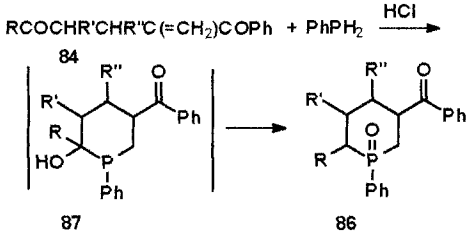
Hydroxyl groups in the 2,5-positions of **81** are *trans,* whereas, in the six-membered rings, the 2,6-hydroxyls are *cis* (see compounds **23,26**, for example). Consequently, ring closure in five- and six-membered cycles has opposite stereochemistry.

Some other 1,4-diketones also react with **79** to give 2,5-dihydroxyphospholanes [17]. Similarly, 1,5-diketones and reagent **79** form 2,6-dihydroxyphosphorinanes **82** and phosphorylated dihydropyrans **83** [18,19]:

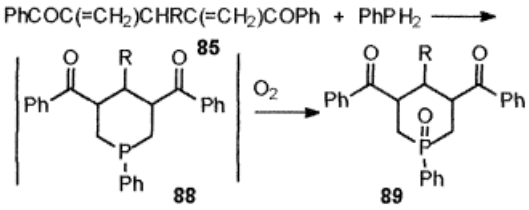


Reaction of 2-Methylene- and 2,4-Dimethylene-1,5-diketones with Phenylphosphine and Phosphonous Acid Esters

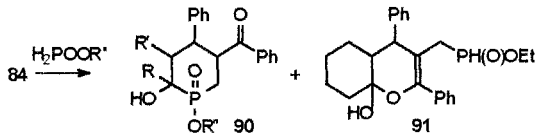
2-Methylene-1,5-diketones **84** and 2,4-dimethylene-1,5-diketones **85** can be synthesized from 1,5-diketones by the Mannich reaction and subsequent deamination [20,21]. Compounds **84** and phenylphosphine in the presence of acid are converted into 3-benzoylphosphorinanes **86** after hydroxyphosphine-phosphine oxide rearrangement of intermediates **87** [22,23]:



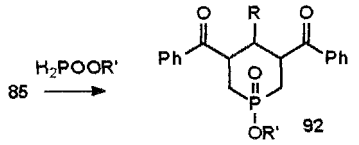
Compounds **85** in reaction with phenylphosphine generate 3,5-dibenzoylphosphorinanes **88**, which can be oxidized by oxygen of the air to oxides **89** [23]:



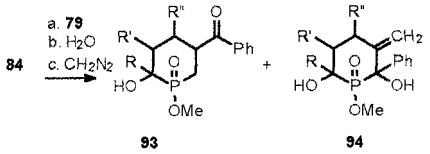
These reactions are not stereoselective; some stereoisomers are obtained in each case. Compounds **84** and **85** react with alkyl hypophosphites without use of a catalyst [24,25]. 5-Benzoyl-2-hydroxyphosphorinanes **90** are obtained as main products from **84**; hemiacetal **91** was obtained as a side product in one case.



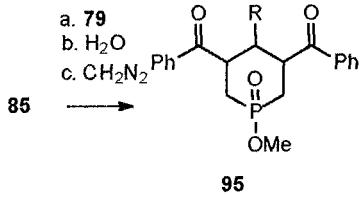
Compound **91** is converted into **90** by boiling in benzene. Alkyl hypophosphites can be added to ethylenic bonds of dimethylene-diketones **85** to form the stereoisomers of 3,5-dibenzoylphosphorinanes **92** [25]:



The reaction of **79** with 2-methylene-1,5-diketones **84** gave phosphorinanes **93** and **94** after hydrolysis and methylation by diazomethane [26,27]:



The reactions of compound **79** with 2,4-dimethylenediketones **85** lead to 2,4-dibenzoylphosphorinanes **95** under the same conditions [28,29]:



Compounds **93** and **95** were obtained in several stereoisomeric forms. The stereoisomers with axial benzoyl groups were converted into stereoisomers with equatorial benzoyl groups in alkaline media.

Experimental Section

General. Melting points are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker WM-250 spectrometer. IR spectra were recorded with a Specord 75-IR spectrometer. Molecular masses of compounds were measured on an LKB 9000S spectrometer at 75 eV.

Stereoisomeric 2-Hydroxyl-1-oxo-1,2-diphenyldecahydrophosphinolines (**38a,b**) *[6].* A solution of diketone **12** (41.0 g, 0.18 mol) and phenylphosphine (19.8 g, 0.18 mol) in acetic acid (180 mL) and hydrochloric acid (75 mL) was refluxed for 15 hours under Ar. The reaction mixture was poured into water (500 mL) and extracted with $CHCl_3$ (4 × 150 mL). After the combined organics had been washed with H_2O and dried ($CaCl_2$), part of the $CHCl_3$ was removed by evaporation. The resulting $CHCl_3$ solution was kept at 0 °C (24 hours). Crystals of **38a** (28.1 g, 46%) were separated; the filtrate was evaporated to give a residue that was chromatographed on silica gel with $CHCl_3$–CH_3COCH_3 (4:1) as eluent to give **38a** (5.5 g, 9%) and **38b** (13.5 g, 22%).

38a: Total yield 55%; mp 237–239 °C. IR (nujol): 3200 (OH), 1185 cm^{-1} (P=O). ^{1}H NMR ($CDCl_3$): δ: 3.77 (C^{2}H, J_{PH} 23.5, J_{HH} 13.1, J_{HH} 4.0 Hz); *m/z* 340 ($M^{+\cdot}$). Anal. calcd for $C_{21}H_{25}O_2P$: C, 74.10; H, 7.40; P, 9.10. Found: C, 74.15; H, 7.59; P, 9.01. Compound **38a** after first melting at 237–239 °C crystallizes to give a product that melts at 245–250 °C. The latter crystals melt at 272–276 °C [288–289 °C after crystallization (ethanol)]; this compound is identical with **38b**.

38b: Mp 288–289 °C. IR (nujol): 3250 (OH), 1155 cm^{-1} (P=O). ^{1}H NMR ($CDCl_3$): δ 3.72 (C^{2}H, J_{PH} 5.6, J_{HH} 13.3, J_{HH} 4.0 Hz); *m/z* 340 ($M^{+\cdot}$). Anal. calcd for $C_{21}H_{25}O_2P$: C, 74.10; H, 7.40; P, 9.10. Found: C, 73.69; H, 7.37; P, 9.17.

2,6-Dihydroxy-1-oxo-1,2,4,6-tetraphenylphosphorinane **55** *[6].* A solution of diketone **9** (16.4 g, 0.05 mol) and phenylphosphine (6.5 g, 0.06 mol) in acetic acid (75 mL) was heated at 90 °C for 6 hours under Ar. After cooling, the mixture was stored at room temperature in the air (48 hours). Water (20 mL) was added, and crystals of **55** (7.5 g, 33%) were separated.

55: Mp 219–221 °C. IR (KBr): 2770 (OH), 1160 cm^{-1} (P=O). Anal. calcd for $C_{29}H_{27}O_3P$: C, 76.64; H, 5.99; P, 6.81. Found: C, 76.52; H, 6.06; P, 6.81.

A solution of $SOCl_2$ (2 mL) in pyridine (6 mL) was added to a suspension of **55** (1 g) in pyridine (5 mL) at 0 °C. The precipitate of pyridine hydrochloride was filtered off, and the filtrate was diluted with water (100 mL). The cyclosulfite **57** (1.1 g, 99%) was collected.

57: Mp 182–185 °C. IR (nujol): no hydroxyl absorption, 1245 (P=O), 1207, 1033 cm^{-1} (S=O, S–O). Anal. calcd for $C_{29}H_{25}O_4PS$: C, 69.59; H, 5.03; P, 6.19. Found: C, 69.71; H, 5.03; P, 5.84.

(*4-Oxo-1,4-diphenylbutyl*)*diphenylphosphine Oxide* **58** *[9].* A solution of diketone **4** (3.58 g, 15

mmol) and diphenylphosphine (5.58 g, 30 mmol) in dioxane (20 mL) and hydrochloric acid (5 mL) was refluxed for 6 hours under argon. The reaction mixture was cooled, water (40 mL) was added, and the reaction products were extracted with $CHCl_3$ (4 × 25 mL). The combined extracts were washed with H_2O, dried, and evaporated to give **58** (5.79 g, 91%).

58: Mp 181–183 °C. IR (nujol): 1682 (C=O), 1172 cm^{-1} (P=O). Anal. calcd for $C_{28}H_{25}O_2P$: C, 79.24; H, 5.94; P, 7.30. Found: C, 79.16; H, 6.15; P, 7.32.

1,2,3-Trihydroxy-2-oxo-3-t-butyl-2-phospha-bicyclo[3.3.0]octane **72** *[12].* Diketone **71** (9.0 g, 50 mmol) and H_3PO_2 (5.0 g, 75 mmol) were heated in a sealed tube (75 °C, 15 hours). The reaction mixture was triturated with H_2O, and **72** (8.4 g, 68%) was obtained as white crystals.

72: Mp 179–181 °C. IR (nujol): 3200 cm^{-1} (OH). Anal. calcd for $C_{11}H_{21}O_4P$: C, 53.22; H, 8.53; P, 12.48. Found: C, 53.01; H, 8.56; P, 12.63.

1,2,5-Trihydroxy-1-oxo-2,3,5-triphenylphospholane **81** *[16].* A solution of diketone **80** (1.0 g, 3.2 mmol) and bis(trimethylsilyl) phosphonite **79** (3.8 g, 18 mmol) in dioxane (30 mL) was stirred under argon at room temperature for 24 hours, poured into water (100 mL), and a resulting precipitate (**81**, 1.21 g, 99%) was collected.

81: Mp 205–207 °C. IR ($CHCl_3$): 3500–3300, 2600–2200, 1800–1600 cm^{-1} (OH, P–O–H). ^1H NMR (DMSO-d6): δ: 2.10 (H^4), 3.02 (H'^4), 3.95 (H^3); J (Hz) 13.0 ($H^4H'^4$), 4.5 (H^3H^4), 13.0 ($H^3H'^4$), 28.0 (H^4P). ^{13}C NMR (DMSO-d6): δ: 76.61 (C^2, J_{CP} 89.3 Hz), 49.17 (C^3, J_{CP} 22.0 Hz), 42.63 (C^3, J_{CP} 16.35 Hz), 74.87 (C^4, J_{CP} 92.5 Hz). Anal. calcd for $C_{22}H_{21}O_4P$: C, 69.47; H, 5.57; P, 8.14. Found: C, 69.76; H, 5.77; P, 8.25.

Stereoisomeric 5-Benzoyl-1-oxo-1,2,4-triphenylphosphorinanes **86a,b** (*R = R″ = Ph, R′ = H*) *[23].* A solution of methylenediketone **84** (R = R″ = Ph, R′ = H) (5.0 g, 15 mmol) and phenylphosphine (2.0 g, 18 mmol) in dioxane (30 mL) and hydrochloric acid (10 mL) was refluxed under argon for 20 hours. The reaction mixture was poured into water (150 mL) and extracted with $CHCl_3$. The extract was washed, dried, and $CHCl_3$ was evaporated. The residue was chromatographed on silica gel with C_6H_{14}–$CHCl_3$ (1:1) as eluent to give **86a** (2.5 g, 39%) and **86b** (2.2 g, 33%).

86a: Mp 263–264 °C. IR (nujol): 1687 (C=O), 1210 cm^{-1} (P=O). ^1H NMR ($CDCl_3$): δ 3.34 (H^2_a), 2.36 (H^3_e), 3.09 (H^3_a), 3.51 (H^4_a), 4.79 (H^5_a), 2.36 (H^6_e), 2.44 (H^6_a). J (Hz) 3.5 ($H^3_eH^2_a$), 13.0 ($H^3_aH^2_a$), 12.0 ($H^3_aH^4_a$), 11.0 ($H^4_aH^5_a$), 3.5 (H^2_aP), 4.0 (H^5P). Anal. calcd for $C_{30}H_{27}O_2P$: C, 79.92; H, 6.04; P, 6.88. Found, %: C, 79.82; H, 6.23; P, 6.67.

86b: Mp 269 °C. IR (nujol): 1680 (C=O), 1210 cm^{-1} (P=O). ^1H NMR ($CDCl_3$) δ: 3.87 (H^2_a), 2.40 (H^3_e), 2.40 (H^3_a) 3.56 (H^4_a), 4.41 (H^5_a), 2.76 (H^6_a), 2.66 (H^6_e). J (Hz) 4.5 ($H^3_eH^2_a$), 11.5 ($H^3_aH^2_a$), 11.5 ($H^3_aH^4$), 11.0 (H^4H^5), 3.7 ($H^5_aH^6_e$), 12.5 ($H^5_aH^6_a$), 20.5 (H^2P), 4.3 (H^5P), 17.1 (H^6_eP), 15.1 (H^6_aP). Anal. calcd for $C_{30}H_{27}O_2P$: C, 79.92; H, 6.04; P, 6.88. Found: C, 80.50; H, 6.15; P, 6.35.

Stereoisomeric 5-Benzoyl-2-hydroxy-1-methoxy-1-oxo-2,4-diphenylphosphorinanes **93a–c** *and 2,6-Dihydroxy-1-methoxy-3-methylene-1-oxo-2,4,6-triphenylphosphorinanes* **94a,b** *[27].* To a solution of diketone **84** (R = Ph) (1.0 g, 3 mmol) in dioxane (10 mL) heated to 70–80 °C was added carefully a solution of phosphonite **79** (2.1 g, 10 mmol) in dioxane (5 mL) under argon. The reaction mixture was stirred (room temperature, 10 minutes) and poured into 2% HCl (100 mL). The organic components were extracted ($CHCl_3$). The extract was washed (H_2O), dried ($MgSO_4$), and the volatiles were removed in vacuo to give a pale yellow oil. This oil was dissolved in ether (15 mL) and an ether solution of CH_2N_2 was added until N_2 evolution ceased. The product of methylation was chromatographed (silica gel L 100/250 mm, ether–methanol, 50:1 → 15:1) and compounds **93a** (0.29 g, 23%), **93b** (0.30 g, 23%), **94a** (0.063 g, 5%), and **94b** (0.06 g, 4%) were obtained.

93a: Mp 124–125 °C. IR (nujol): 3238 (OH), 1690 (C=O), 1240 cm^{-1} (P=O). ^1H NMR ($CDCl_3$) δ 3.39 ($POC\underline{H}_3$), 3.92 (H^3_a), 2.24 (H^3_e), 3.81 (H^4), 4.22 (H^5), 2.74 (H^6_a), 2.35 (H^6_e); J (Hz): 13.5 ($H^3_aH^3_e$), 13.0 ($H^3_aH^4$), 3.5 ($H^3_eH^4$), 3.0 (H^4H^5), 7.0 ($H^5H^6_a$), 1.0 ($H^5H^6_e$), 3.0 (H^3_aP), 28.5 (H^3_eP), 28.5 (H^5P). Anal. calcd for $C_{25}H_{25}O_4P$: C, 71.42; H, 5.99; P, 7.37. Found: C, 71.65; H, 5.70; P, 7.67.

93b: Mp 194–196 °C. IR (nujol): 3240 (OH), 1694 (C=O), 1220 cm^{-1} (P=O). ^1H NMR ($CDCl_3$) δ: 3.28 ($POCH_3$), 3.73 (H^3_a), 2.36 (H^3_e), 3.86 (H^4), 4.38 (H^5), 2.73 (H^6_a), 2.47 (H^6_e); J (Hz) 14.0 ($H^3_aH^3_e$), 13.0 ($H^3_aH^4$), 3.0 ($H^3_eH^4$), 5.0 (H^4H^5), 6.5 ($H^5H^6_a$), 6.0 ($H^5H^6_e$), 3.0 (H^3_aP), 29.5 (H^3_eP), 25.5 (H^5P). Anal. calcd for $C_{25}H_{25}O_4P$: C, 71.42; H, 5.99; P, 7.37. Found: C, 71.05; H, 6.25; P, 7.21.

94a: Mp 127–129 °C. IR (nujol): 3280 (OH), 1244 cm^{-1} (P=O). ^1H NMR ($CDCl_3$) δ: 3.23 ($POCH_3$), 4.61, 4.76 (=CH_2). Anal. calcd for $C_{25}H_{25}O_4P$: C, 71.42; H, 5.99; P, 7.37. Found: C, 71.64; H, 6.26; P, 7.21.

94b: Mp 183–186 °C. IR (nujol): 3476 (OH), 1194 cm^{-1} (P=O). ^1H NMR ($CDCl_3$) δ: 3.67 ($POCH_3$), 4.82, 5.24 (=CH_2). Anal. calcd for $C_{25}H_{25}O_4P$: C, 71.42; H, 5.99; P, 7.37. Found: C, 71.33; H, 6.18; P, 7.56.

To a solution of **93a** (50 mg) in $CHCl_3$ (5 mL) was added a solution of KOH (20 mg) in methanol (0.2

mL). After having been stirred at room temperature for 2 hours, the reaction mixture was washed (H_2O), and $CHCl_3$ was evaporated. The residue was triturated with ether (0.5 mL) to give **93c** (33 mg, 66%).

93c: Mp 170–172 °C. IR (nujol): 3156 (OH), 1687 (C=O), 1236 cm^{-1} (P=O). ^1H NMR ($CDCl_3$) δ: 3.43 ($POCH_3$), 2.93 (H_a^3), 2.23 (H_e^3), 3.83 (H^4), 4.56 (H^5), 2.61 (H_a^6), 2.07 (H_e^6); *J* (Hz) 14.0 ($H_a^3H_e^3$), 12.5 ($H_a^3H^4$), 3.0 ($H_e^3H^4$), 11.5 (H^4H^5), 13.5 ($H^5H_a^6$), 2.9 ($H^5H_e^6$), 2.0 (H_a^3P), 17.5 (H_e^3P), 5.0 (H^5P). Anal. calcd for $C_{25}H_{25}O_4P$: C, 71.42; H, 5.99; P, 7.37. Found: C, 71.68; H, 6.04; P, 7.40.

ACKNOWLEDGMENT

The author is grateful to the Russian Fund of Fundamental Exploration for the support of our investigation.

REFERENCES

[1] S. A. Buckler, M. Epstein, *Tetrahedron, 18,* 1962, 1211.
[2] M. Epstein, S. A. Buckler, *Tetrahedron, 18,* 1962, 1231.
[3] S. M. Kalinov, M. F. Rostovskaya, V. I. Vysotskii, *Zhurnal Obschei Khimii (Russian J. General Chem., ZhOKh), 58,* 1988, 783.
[4] V. I. Vysotskii, M. F. Rostovskaya, *ZhOKh, 56,* 1986, 1046.
[5] V. I. Vysotskii, S. M. Kalinov, M. N. Tilichenko, *ZhOKh, 50,* 1980, 1707.
[6] V. I. Vysotskii, V. V. Isakov, S. M. Kalinov, T. V. Khaidukova, M. N. Tilichenko, *ZhOKh, 53,* 1983, 2206.
[7] V. I. Vysotskii, E. V. Pavlycheva, M. N. Tilichenko, *ZhOKh, 45,* 1975, 1466.
[8] V. G. Kostin, E. S. Karaulov, M. N. Tilichenko, *ZhOKh, 50,* 1980, 2384.
[9] M. F. Rostovskaya, S. M. Kalinov, V. I. Vysotskii, *ZhOKh, 60,* 1990, 2691.
[10] S. M. Kalinov, V. I. Vysotskii, M. N. Tilichenko, *ZhOKh, 51,* 1981, 1673.
[11] Ch. Marie, *Ann. Chim Phys., 3,* 1904, 335.
[12] Yu. V. Prikhod'ko, A. S. Skobun, M. F. Rostovskaya, V. I. Vysotskii, *ZhOKh, 61,* 1991, 1263.
[13] V. I. Vysotskii, A. S. Skobun, M. N. Tilichenko, *ZhOKh, 48,* 1978, 2442.
[14] V. I. Vysotskii, A. S. Skobun, M. N. Tilichenko, *ZhOKh, 49,* 1979, 329.
[15] V. I. Vysotskii, A. S. Skobun, M. N. Tilichenko, *ZhOKh, 49,* 1979, 1956.
[16] V. I. Vysotskii, S. V. Biryukov, M. F. Rostovskaya, B. K. Vasiliev, S. V. Lindeman, Yu. T. Struchkov, *ZhOKh, 61,* 1991, 391.
[17] S. V. Biryukov, M. F. Rostovskaya, V. I. Vysotskii, *ZhOKh, 65,* 1995, 598.
[18] V. I. Vysotskii, S. V. Levan'kov, Yu. V. Prikhod'ko, *ZhOKh, 59,* 1989, 2223.
[19] V. I. Vysotskii, S. V. Levan'kov, *ZhOKh, 61,* 1991, 1315.
[20] G. V. Pavel, M. N. Tilichenko, *Zhurnal Organicheskoi Khimii (Russian J. Organic Chem., ZhOrKh), 2,* 1966, 2262.
[21] G. V. Pavel, M. N. Tilichenko, *ZhOrKh, 4,* 1968, 1420.
[22] Yu. V. Prikhod'ko, V. I. Vysotskii, G. V. Pavel, M. N. Tilichenko, *ZhOKh, 54,* 1984, 1427.
[23] V. I. Vysotskii, Yu. V. Prikhod'ko, G. V. Pavel, M. N. Tilichenko, *ZhOKh, 60,* 1990, 1282.
[24] V. I. Vysotskii, Yu. V. Prikhod'ko, G. V. Pavel, M. N. Tilichenko, *ZhOKh, 53,* 1983, 2645.
[25] V. I. Vysotskii, Yu. V. Prikhod'ko, G. V. Pavel, M. N. Tilichenko, *ZhOKh, 55,* 1985, 2475.
[26] V. I. Vysotskii, A. G. Vilitkevich, *ZhOKh, 63,* 1993, 358.
[27] V. I. Vysotskii, A. G. Vilitkevich, *ZhOKh, 65,* 1995, 782.
[28] V. I. Vysotskii, A. G. Vilitkevich, I. I. Zhdamirova, *ZhOKh, 63,* 1993, 1530.
[29] V. I. Vysotskii, A. G. Vilitkevich, ZhOKh, *66,* 1996, 233.