SYNTHESIS OF 5-METHYL-2-ETHYL-4-CHLORO-2-OXO-

1,2-OXA-4-PHOSPHOLENE

A.N. Pudovik, V.K. Khairullin, and R.M. Kondrat'eva UDC 542.91+661.718.1

The reaction of alkyldichlorophosphines with biacetyl proceeds with a cleavage of hydrogen chloride and the formation of 5-methyl-2-alkyl-4-chloro-2-oxo-1,2-oxa-4-phospholenes [1] (Scheme b). Phenyldichlorophosphine reacts in a similar manner with biacetyl [2].

In order to verify the validity of the scheme proposed by us for the progress of these interesting reactions we report in the present paper the counter synthesis of 5-methyl-2-ethyl-4-chloro-2-oxo-1,2-oxa-4-phospholene (III). The starting 5-methyl-2-ethyl-2-oxo-1,2-oxa-4-phospholene (I) was obtained by us by the known procedure (Scheme a) [3-5], which consists in the reaction of the acid chlorides of trivalent phosphorus with α , β -unsaturated ketones in the presence of acetic anhydride. The IR spectrum of (I) contains the absorption bands of the P=O group at 1220 cm⁻¹ and of the $C=C_{ring}$ at 1680 cm⁻¹ (Fig. 1, 1). As the result of the chlorination of oxa-4-phospholene (I) we obtained 5-methyl-2-ethyl-4,5-dichloro-2-oxo-1,2-oxaphospholane (II), which when treated with triethylamine in benzene is easily dehydrochlorinated with the formation of 5-methyl-2-ethyl-4-chloro-2-oxo-1,2-oxa-4-phospholene (III). The constants and IR spectrum of (III) are identical with the constants and IR spectrum of the oxa-4-phospholene (III) obtained by us previously by the reaction of ethyldichlorophosphine with biacetyl [1] (see Scheme b). Also identical were the constants and IR spectra of the products of the further transformations of (III), the ethyl ester of ethyl- $(\beta$ -chloro- γ -oxobutyl) phosphinic acid (IV) and 5-methyl-2-ethyl-4,4,5-trichloro-2-oxo-1,2-oxaphospholene (V), whose constants and IR spectrum were identical with the constants and IR spectrum of the (IV) and (V) obtained by us previously [1]. Oxaphospholane (V) is easily dehydrochlorinated when it is treated with 2 moles of triethylamine in benzene. Here are formed triethylamine hydrochloride and 2-ethyl-5-methylene-4-chloro-2-oxo-1,2-oxa-3-phospholene (VI), which contains a conjugated system of C = C double bonds, found in the s-trans conformation. Oxa-3-phospholene (VI) has an unusually high value of n_D^{20} 1.5290, which exceeds the n_D^{20} of benzene. The IR spectrum of (VI) is interesting. In it are present the absorption band of the P = P group at 1220 cm⁻¹, and the very intense absorption bands of $\nu_C = C_{ring}$ at 1540 and of

 $\nu_{\rm C} = C_{\rm exocyclic}$ at 1660 cm⁻¹, comparable in intensity to the absorption of the carbonyl group. Also very intense are the absorption bands of the hydrogens on the carbon attached to the double bond in 3050 and 3080 cm⁻¹ region (Fig. 1, 2).

In connection with the studies made by us it was very interesting to also synthesize some other oxa-3-phospholenes with a conjugated system of double bonds, not containing chlorine atoms. As the result of the reaction of either ethyl- or phenyldichlorophosphine with methyl isopropenyl ketone in the presence of acetic anhydride we obtained the 4,5-dimethyl-2-ethyl- (VII) and 4,5-dimethyl-2-phenyl-2-oxo-1,2-oxa-4-phospholenes (VII). The IR spectrum of (VII) (Fig. 1, 3) is in agreement with the structure assigned to it. Oxa-4-phospholenes (VII) and (VIII) are readily chlorinated at room temperature with the formation of oxa-phospholanes (IX) and (X). The treatment of compounds (IX) and (X) with 2 moles of triethylamine in an inert solvent gave the 4-methyl-2-ethyl- (XI) and 4-methyl-2-phenyl-5-methylene-2-oxo-1,2-oxa-3-phospholenes (XII). Oxa-3-phospholene (XI) also has a high value of n_D^{20} 1.5170. In its IR spectrum are present the absorption band of the P=Ogroup at 1265 cm⁻¹ and the very intense absorption bands of $\nu_{\rm C=Cring}$ at 1540 and of

 $\nu_{\rm C} = C_{\rm exocyclic}$ at 1645 cm⁻¹, and of the hydrogens on the carbon attached to the double bonds at 3080 cm⁻¹ (Fig. 1, 4).

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Com- pound No.	Formula	Yield, 🌾	Bp, °C (p, mm of Hg)	d_4^{20}	n_D^{20}			Found Calcd.		, %
						found	calcd.	с	н	Р
XIII	$\begin{array}{c} O & O \\ \parallel \\ C_2H_5 - P - CH = C - C - CH_3 \end{array}$	100,0	_	1,1582	1,4906	44,06	44,60	47,78 47,72	$\frac{7,21}{7,44}$	17,76 17,59
XIV	ÓH ĊH ₃ O O C ₂ H ₅ ^H CHCHCH-3 OCH, CH ₃	95,0	80—81 (0,006)	1,0775	1,4750	53,36	53,95	52,91 52,93	8,23 8,39	<u>15,32</u> 15,17
XV	$\begin{array}{c} 0 \\ C_2H_3 - P - CH = C - C - CH_3 \\ 0 \\ C_3H_7 \\ CH_3 \end{array}$	89,0	92(0,005)	1,0567	1,4740	58,04	58,57	54,63 55,03	$\frac{8,75}{8,78}$	14,30 14,20
XVI	O O CeH _s -P-CH=C-C-CH _s OC ₄ H, CH ₃	79,0	139(0,04)	1,0901	1,5180	77,91	77,86	64,61 64,29	$\frac{7,29}{7,55}$	11,22 11,05

TABLE 1. Phosphorylation of α , β -Unsaturated Ketones

Oxa-3-phospholenes (XI) and (XII) are very reactive compounds. They easily react with water and alcohols to give phosphorylated α , β -unsaturated ketones (XIII)-(XVI).

The IR spectrum of the ethyl ester of ethyl-(3-keto-2-methyl-butenyl)phosphinic acid (XIV) contains the absorption bands of the P=O group at 1200, of C=C at 1628, and of C=O at 1689 cm⁻¹.

EXPERIMENTAL METHOD

The IR spectra were taken on a UR-10 spectrometer. A drop of the substance was pressed between two KBr plates. The layer thickness was not controlled.

 $\frac{2-\text{Methyl-2-ethyl-2-oxo-1,2-oxa-4-phospholene (I).}{2} \text{ To a stirred mixture of 21 g of methyl vinyl ketone and 30.6 g of acetic anhydride at 0-5°, in a dry N₂ atmosphere, was added 39.2 of ethyldichlorophosphine in drops. After stirring at room temperature for 24 h we distilled off 36 g of CH₃COCl (bp 52-53°, n_D²⁰ 1.3900). Distillation of the residue gave 24 g (54.5%) of oxa-4-phospholene (I) as an oily liquid with bp 67° (0.006 mm); 125° (10 mm); d₄²⁰ 1.1247; n_D²⁰ 1.4782. Found: C 49.09; H 7.56; P 20.86%. MR 36.89. C₆H₁₁O₂P. Calculated: C 49.31; H 7.58; P 21.20%; MR 36.98.$

5-Methyl-2-ethyl-4,5-dichloro-2-oxo-1,2-oxaphospholane (II). Into a solution of 15.5 g of (I) in 100 ml of CCl₄ at $0-5^{\circ}$ was passed dry chlorine gas until the temperature ceased to rise.

At the start the CCl_4 was removed using a water-jet pump, and then using a high vacuum. The residue, phospholane (II), 23 g (100%), represented a thick oily liquid; d_4^{20} 1.3655; n_D^{20} 1.5050. Found: C 32.81; H 4.94; Cl 33.10; P 13.82%, MR 47.14. $C_6H_{11}Cl_2O_2P$. Calculated: C 33.20; H 5.11; Cl 32.67; P 14.27%, MR 47.19.

 $\frac{5-\text{Methyl-2-ethyl-4-chloro-2-oxo-1,2-oxa-4-phospholene (III)}{2} \text{ To 20.5 g of (II) in 150 ml of benzene} at 0° was added 9.6 g of (C₂H₅)₃N in drops. After 12 h the (C₂H₅)₃N·HCl was filtered (15.5 g), and the benzene was distilled off. Distillation of the residue gave 9 g (50.5%) of oxa-4-phospholene (III), bp 92° (0.005 mm); d²⁰₄ 1.2520; n²⁰_D 1.4990. Found: C 40.13; H 5.68; Cl 19.15; P 16.91%, MR 42.30. C₆H₁₀ClO₂P. Calculated: C 39.90; H 5.58; Cl 19.63; P 17.15%; MR 41.85. The compound was obtained as an oily liquid that turned dark when stored.$

Ethyl Ester of Ethyl-(β -chloro- γ -oxobutyl)phosphinic Acid (IV). In an Arbuzov flask were placed 5 ml of absolute ethanol and 9 g of (III). The temperature of the reaction mixture rose from 20 up to 56°. After removal of the excess alcohol in vacuo the residue was distilled. We obtained 6.5 g (57%) of ester (IV) with bp 92° (0.02 mm); d_4^{20} 1.1558; n_D^{20} 1.4680. From [1]: bp 100° (0.09 mm); d_4^{20} 1.1578; n_D^{20} 1.4675.

5-Methyl-2-ethyl-4,4,5-trichloro-2-oxo-1,2-oxaphospholane (V). Into a solution of 8.7 g of 4-phospholene (III) in 70 ml of CCl_4 , with cooling, was passed dry chlorine gas. After removal of the CCl_4 in vacuo we obtained 12.2 g (100%) of phospholane (V) with mp 56-59°. From [1]: mp 56-59°.

<u>2-Ethyl-5-methylene-4-chloro-2-oxo-1,2-oxa-3-phospholene (VI)</u>. To a solution of 12.2 g phospholane (V) in 100 ml of absolute benzene, with stirring, was added 9.8 g of $(C_2H_5)_3N$ in drops. The formed triethylamine hydrochloride (12.7 g) was filtered, and the benzene was removed in vacuo. Distillation of the residue gave 5.8 g (63.5%) of 3-phospholene (VI) with bp 90° (0.02 mm); d_4^{20} 1.2906; n_D^{20} 1.5290. Found: Cl 20.17; P 17.04%; MR 41.86. $C_6H_8ClO_2P$. Calculated: Cl 19.86; P 17.35%; MR 42.28.

4,5-Dimethyl-2-ethyl-2-oxo-1,2-oxa-4-phospholene (VII). A four-necked flask, fitted with a stirrer, thermometer, calcium chloride tube and a dropping funnel, was filled with dry CO₂, after which 46.5 g of ethyldichlorophosphines and 31.6 g of acetic anhydride were added. With cooling of the flask in an ice-salt mixture, 28.8 g of methyl isopropenyl ketone was added in drops at such a rate that the temperature of the reaction mixture remained in the range 0-10°. After 12 h the calcium chloride tube was replaced by a descending condenser and 44 g (80%) of CH₃COCl was distilled off, bp 53° and n_D^{20} 1.3900. Distillation of the residue gave 44 g (77.3%) of 4-phospholene (VII) with bp 73° (0.007 mm); d_4^{20} 1.0970; n_D^{20} 1.4810. Found: C 52.16; H 8.41; P 19.45%; MR 41.55. C₇H₁₃O₂P. Calculated: C 52.49; H 8.18; P 19.35%; MR 41.61.

 $\frac{4,5-\text{Dimethyl-2-phenyl-2-oxo-1,2-oxa-4-phospholene (VIII)}{\text{of 89.5 g of phenyldichlorophosphine, 51 g of acetic anhydride and 42.5 g of methyl isopropenyl ketone. The yield of (VIII) was 60.5 g (57.8%); bp 152° (0.02 mm); d_4^{20} 1.1735; n_D^{20} 1.5522$. Found: C 63.13; H 6.24; P 15.01%; MR 56.65. C₁₁H₁₃O₂P. Calculated: C 63.46; H 6.25; P 14.90%, MR 56.47.

4,5-Dimethyl-2-ethyl-4,5-dichloro-2-oxo-1,2-oxaphospholane (IX). Into a solution of 24.5 g of 4phospholene (VII) in 100 ml of CCl₄, with cooling, was passed dry chlorine gas until the temperature of the reaction mixture ceased to rise. The CCl₄ was vacuum-distilled, while the residue was distilled using a high vacuum. We obtained 34.5 g (98.5%) of phospholane (IX); d_4^{20} 1.3308; n_D^{20} 1.5055. Found: C 35.93; H 5.64; Cl 30.18; P 13.53%. MR 51.54. C₇H₁₃Cl₂O₂P. Calculated: C 36.38; H 5.67; Cl 30.69; P 13.41%; MR 51.81.

4,5-Dimethyl-2-phenyl-4,5-dichloro-2-oxo-1,2-oxaphospholane (X). Obtained in a similar manner by the passage of chlorine into a solution of 50 g of phospholene (VIII) in 150 ml of CCl₄. We obtained 67 g (100%) of (X); d_4^{20} 1.3857; n_D^{20} 1.5650. Found: C 47.61; H 4.97; P 10.71%; MR 66.12. $C_{11}H_{13}Cl_2O_2P$. Calculated: C 47.32; H 4.69; P 11.06; MR 66.67.

 $\frac{4-\text{Methyl-2-ethyl-5-methylene-2-oxo-1,2-oxa-3-phospholene (XI)}{2}.$ In a flask fitted with a stirrer were placed 300 ml of absolute benzene, 34.5 g of phospholane (IX) and 30 g of triethylamine. After 12 h the (C₂H₅)₃N·HCl was filtered and the benzene was distilled off. Distallation of the residue gave 18.5 g (78.5%) of 3-phospholene (XI) with bp 81.5° (0.006 mm); d²⁰₄ 1.1265; n²⁰₂ 1.5170. Found: C 52.68; H 7.16; P 19.55%; MR 42.27. C₇H₁₁O₂P. Calculated: C 53.16; H 7.01; P 19.59%; MR 42.05.



Fig. 1. Infrared spectra: 1) 5-methyl-2-ethyl-2-oxo-1, 2-oxa-4-phospholene (I); 2) 2-ethyl-5-methylene-4chloro-2-oxo-1,2-oxa-3-phospholene (VI); 3) 4,5-dimethyl-2-ethyl-2-oxo-1,2-oxa-4-phospholene (VII); 4) 4-methyl-2-ethyl-5-methylene-2-oxo-1,2-oxa-3-phospholene (XI); 5) ethyl ester of ethyl-(3-keto-2-methylbutenyl)phosphinic acid (XIV).

 $\frac{4-\text{Methyl-2-phenyl-5-methylene-2-oxo-1,2-oxa-3-phospholene (XII)}{\text{reflux condenser were placed 67 g of phospholane (X), 200 ml of anhydrous dioxane and 48.5 g of (C₂H₅)₃N, and the mixture was heated at 80° for 2 h. After cooling, the (C₂H₅)₃N·HCl was filtered and the dioxane was vacuum-distilled. Distillation of the residue gave 37 g (74.8%) of 3-phospholene (XII) with bp 125-127° (0.02 mm); d_4^{20} 1.1866; n_D^{20} 1.5640. Found: C 63.58; H 5.38; P 15.03%, MR 56.91.$

Ethyl-(3-keto-2-methylbutenyl)phosphinic Acid (XIII). To 3.16 g of 3-phospholene (XI) was added 0.5 g of water. Here the temperature of the reaction mixture rose from 20 up to 48°. After removal of the excess water in a high vacuum we obtained 3.5 g of (XIII) (see Table 1).

Esters of Ethyl- (or Phenyl-)(3-keto-2-methylbutenyl)phosphinic Acid. An equimolar mixture of either 3-phospholene (XI) or (XII) and the appropriate alcohol was sealed in an ampul and heated at 100° for 8 h. Distillation gave the ethers (XIV, XV, XVI) (see Table 1).

CONCLUSIONS

1. The counter synthesis of 5-methyl-2-ethyl-4-chloro-2-oxo-1,2-oxa-4-phospholene was accomplished.

2. The 4-methyl-2-ethyl- and 4-methyl-2-phenyl-5-methylene-2-oxo-1,2-oxa-3-phospholenes were obtained by the chlorination and dehydrochlorination of the 4,5-dimethyl-2-ethyl- and 4,5-dimethyl-2-phenyl-2-oxo-1,2-oxa-4-phospholenes.

3. The 4-methyl-2-ethyl (or phenyl)-5-methylene-2-oxo-1,2-oxa-3-phospolenes when treated with water or alcohols are converted to the corresponding phosphorylated α , β -unsaturated ketones.

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